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for May, 1937

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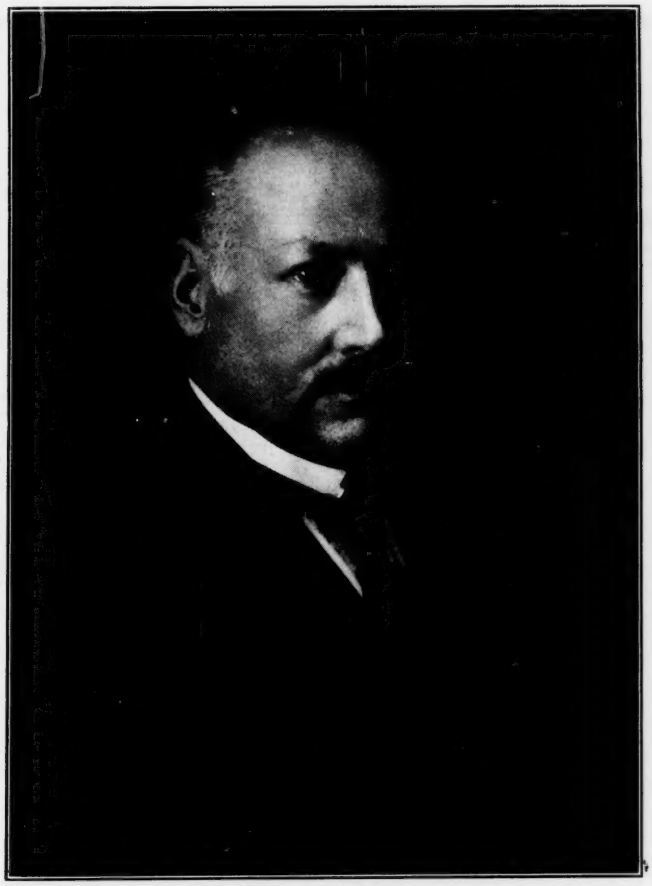

EMIL ABDERHALDEN (1877–)

For biographical note contributed by Dr. Ralph E. Oesper, of the University of Cincinnati, see page 237. Dr. Oesper also lent the photograph here reproduced.

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EDITOR'S OUTLOOK

A MINOR MYSTERY DISPELLED. Recently we have had several inquiries, oral and written, as to the origin and significance of the "remarkable conglomeration" (one correspondent wrote "agglomeration") of symbols which appears on our cover from time to time. The cover design in question is a leaf from the desk of a telephone-pad decorator. The poor fellow is naturally somewhat sensitive on the subject of his affliction, and we have agreed to preserve his anonymity. This statement of origin might seem to obviate the necessity for any discussion of significance, yet there are meanings to be found in the weird scratchings of our unfortunate friend.

Considering first the color plate, one finds in the upper left-hand corner the triangular alchemistic symbols for fire, air, earth, and water, accompanied by the somewhat later symbols for sulfur and phlogiston. Immediately beneath them is another alchemistic device—a seal of Solomon with the symbols for the "seven metals." At the upper center is an elaborate "cross of contraries" modeled after the one that faced the title page of Leibnitz' first book, *Dissertatio de Arte Combinatoria*. [For further information concerning these symbols consult TENNEY L. DAVIS, "Primitive science, the background of early chemistry and alchemy," J. CHEM. EDUC., **12,** 3–10 (1935).]

Continuing with the color plate, the circular designs to the right of the cross of contraries are some of Dalton's atomic symbols [H. F. COWARD, "John Dalton (b. 1766, d. 1844)", *ibid.*, **4,** 22–37 (1927)]. The polygons beneath are reminiscent of von Baeyer's Spannungstheorie [*Ber.*, **18,** 2277 (1885)]. Along the lower half of the right-hand margin are Wislicenus' tetrahedral diagrams for singly, doubly, and triply bonded carbon atoms [*Abh. kgl. Sächs. Ges. der Wissenschaften*, **14,** 1 (1887)]. Beneath the cross of contraries are the Kekulé diagrams for ethylene and benzene [*Z. Chem.*, [2], **3,** 214 (1867); *Ann.*, **137,** 129 (1866)]. At the bottom is Mendeleéff's periodic table in the form in which it appeared on the Mendeleéff memorial in Leningrad [*cf.*, B. N. MENSCHUTKIN, J. CHEM. EDUC., **13,** 373 (1936)]. Incidentally, a reader has called our attention to the fact that the draftsman, in copying, erroneously placed the symbol for lanthanum where that for hafnium should have appeared. The cut has since been corrected.

To the left of the periodic table is a modern version of the Kekulé model for *n*-heptane, and above it are Pasteur's tartrate crystals and the modern structural formulas for the two optically active and the meso tartaric acids.

The black-and-white plate shows, at the upper left, the Bohr orbits of the hydrogen atom, and, at the upper right, bonding and repulsion, respectively, between two pairs of hydrogen atoms. At the upper center there is a perspective projection of an ethylene model. In the plan diagrams from which the projection was made, the relative sizes of the carbon and hydrogen are those calculated as consistent with the moment of inertia derived from spectral data. At the center is a Lane X-ray diffraction pattern, showing the principal spots for rock-salt. To the left are three planes of the layer lattice of graphite, and to the right two layer diagrams of Bragg crystal models. At the lower left-hand corner are the five quantum-mechanical resonance structures of benzene, and at the lower right-hand corner a Fourier projection from the X-ray diffraction pattern of anthracene. In the periodic table, elements discovered since Mendeleéff's time are added in black.

FRITZ HABER

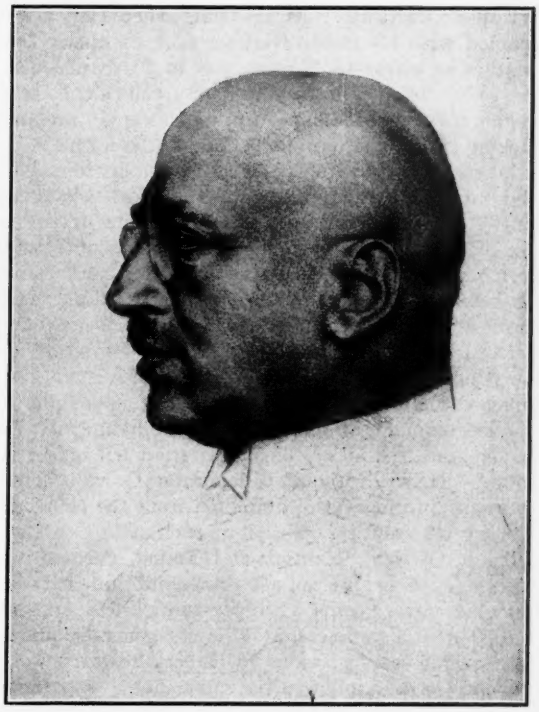
E. BERL

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

ON January 29, 1934, a great man passed from our midst. Fritz Haber was one of those men who made themselves immortal because of their life work—not only in the field of science, but also in the humanities. Haber created a world industry—that of synthetic ammonia. From this, other important, high-pressure industries sprang. The world production of synthetic ammonia for 1935 is estimated at nearly three million metric tons. Besides this great feat, Haber accomplished much other important and fundamental work, more than enough to leave to posterity a name of immortal fame.

Fritz Haber was born on December 9, 1868, in Breslau. He received his doctor's degree, with a dissertation in organic chemistry, under Liebermann who was co-inventor of synthetic alizarine. Haber did not work much in this field later on. Like so many famous men, he was an autodidact. Without being initiated by an older, prominent colleague, he carried out his great research work in the fields of electrochemistry, physical chemistry, technical chemistry, photochemistry, and physics. A decisive point in his life was that in 1894 when he came to Fritz Bunte at Karlsruhe. Bunte at that time and also later was active with Engler in the technical field, especially in the field of fuels. Haber accomplished an important part of his great and extensive research in Karlsruhe.

Wilhelm Ostwald classified scientists in two main groups (which, however, admit of some exceptions): scientists of the romantic type, such as Liebig, Gerhardt, and Alfred Werner who contributed greatly in their youth; scientists of the classical type, such as Faraday, Edison, Gibbs, and Helmholtz who carried out their great researches with almost unimpaired force and breadth of vision during the entire period of their long lives. It is difficult to put Haber in either of these classes. He did not achieve great works before his thirtieth year as most scientists of the romantic type seem to have done. Not until he had reached this age did the development of his personality begin in breadth and depth. In his habilitation thesis which he wrote at twenty-eight we find remarkable statements which are still interesting. Haber was among the first who studied the cracking processes which since have attained such importance. The decomposition of hexane and trimethylethylene by heat and the decomposition of illuminating gas on cooled surfaces were clarified by him. This and perhaps a few other researches he may have carried out at the instigation of Bunte. Soon after began an exceedingly important period, in which Haber was occupied intensively with electrochemical research. In 1898 appeared an introduction to these studies in his book "Grundriss der technischen Elektro-Chemie auf theoretischer Grundlage." Today this book is still of great interest. At that time it was believed that electrochemical processes in the field of oxidation and reduction chemistry would attain great industrial importance. However, the hopes which one had in this direction were only partially realized.



FRITZ HABER

The Faraday law, according to which 96,540 Coulombs per g.-equivalent are to be used for a substance to be transformed, destroyed these expectations somewhat. It is especially to Haber that we owe our enlightenment regarding the complicated processes of the reduction of aromatic nitro compounds in acid and alkaline media.

Engler, who besides his researches in oil, was occupied also with autoxidation problems, incited several valuable contributions of Haber in this particular field at the beginning of this century. Haber took up these again with more profound interest in

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his later years. As happens so frequently, earlier researches formed the basis of later, fully developed scientific work.

From electrochemistry to pure physical chemistry was only a short step for Haber. Beginning with studies of gases, with which he was occupied about eight years previously, he studied gas equilibriums which shortly were destined to bring him to the peak of his scientific and technical attainments. Haber opened a new field in gas reactions, creating the pressure synthesis of ammonia—a monument to science which will outlive the centuries. It is known that the technical pressure synthesis opened a new scientific and technical field, the industrial importance of which cannot be estimated. In passing, it may be mentioned that one of the important uses of pressure synthesis, namely, the hydrogenation of solid and liquid fuels, had its origin also in Haber's Institute. At the time when Haber was occupied with his momentous research on the hydrogenation of nitrogen, Bergius was in Karlsruhe also. The writer ascribes it to this happy coincidence that Bergius conceived the important idea to apply pressure cracking hydrogenation upon solid and liquid fuels.

Haber, occupied with gas reactions, published in 1905 a book on "Thermodynamics of Technical Gas Reactions." This book was published at about the same time that Nernst advanced his third fundamental law of thermodynamics. In studying this important book, one is under the impression that Haber would have discovered the third fundamental law if Nernst had not anticipated him. About that time two Austrian industrialists, the Margulies brothers of Vienna, approached Haber, asking him if it was not possible to produce ammonia from nitrogen and hydrogen over nitrides and hydrides. This suggestion fell on fertile ground. Haber, with his collaborator G. van Oordt, studied the formation of ammonia from the elements. Like several scientists before him, such as Le Chatelier, Wilhelm Ostwald, Ramsay and Young, Perman and Atkinson, Haber determined the equilibrium between ammonia, nitrogen, and hydrogen at high temperatures of 1000°, without pressure. It is not generally known that several years previous to Haber's research work, Wilhelm Ostwald followed the same course, apparently with a good chance of success. By conducting nitrogen and hydrogen over technical iron, he obtained more than traces of ammonia. The tests which were carried out afterwards with iron, which was produced by reduction with hydrogen from iron ores, showed the error in Ostwald's experiments. The Ostwald iron yielded ammonia only as long as it contained nitrides. As soon as the nitrogen of the nitrides was transformed into ammonia, the effect of the iron at normal pressure became nil. The writer knows of a similar case, although of less industrial importance. Scientists asserted that carbon may be converted, without pressure, into methane if the carbon to be hydrogenated is precipitated upon nickel. The nickel acts as catalyst at the hydrogenation reaction. It could be shown, however, that methane was formed only so long as the nickel carbide which was present was converted with hydrogen into methane. If the carbide was decomposed, no further formation of methane took place.

Haber's research work with van Oordt regarding the production of ammonia from the elements was continued with LeRossignol. Their results did not concur with the calculations of Nernst, based upon his third fundamental law, which meanwhile had been published. A discussion started between these two great scholars, in which Nernst called attention to the fact that by increase of pressure the equilibrium of the exothermic nitrogen hydrogenation may be displaced in favor of a larger formation of ammonia. Historically considered, Nernst was the first who, with his collaborator Jost, produced ammonia from the elements at 50 atm. pressure with platinum, iron, and later on with manganese as catalyst at 685°C. Nernst seemed to realize fully the importance of pressure synthesis. According to a story which was told the writer some time ago, Nernst asked a leading German chemical industrialist, who died recently, if it were technically feasible to carry out a reaction at glowing heat and pressure of several hundred atmospheres. The answer was supposed to have been, "This is absolutely impossible." Haber, accustomed to carry out his ideas himself, did not consult a so-called expert, but with his collaborator, LeRossignol, built a small apparatus in which ammonia could be synthesized under pressure. Meanwhile it was found that the chemical constant of the hydrogen was not 2.2, according to Nernst's first estimation, but 1.6. Therefore, Haber's estimations for the NH_3 content in the equilibrium, which Nernst found to be much too high, was somewhat lower than it was established afterwards. Haber, who at first was rather pessimistic regarding the industrial value of the pressure synthesis of ammonia, changed his mind, and thus was opened the field of technical pressure-hydrogenation.

Haber's older colleague, Engler, was also a member of the board of directors of the Badische Anilin und Sodafabrik (now the I. G. Farbenindustrie—A. G.). This concern was interested at that time in nitrogen problems. Experiments were carried out to bind nitrogen of the air by combustion of air and by synthesis of nitrides. Engler aroused the interest of this firm, and Messrs. Bosch and Mittasch were sent to Karlsruhe to inspect the apparatus. It was shown to these gentlemen and, as usual in such cases, it did not function. However, the difficulties were met the same day. From that day on the development of pressure synthesis began. In an exemplary manner Haber not only carried out the thermodynamic investigations, but also invented the so-called circulating system, whereby, under pressure, the nitrogen-hydrogen mixture circulates continuously, fresh gas being added as the reactants are converted into ammonia. Everyone knows of the enormous task accomplished by Bosch with his collaborators, especially with Mittasch and Lappe, in order to overcome the technical difficulties of the process.

Haber proposed osmium as an excellent catalyst. It was established very soon that the world supply of osmium amounted only to a few kilograms and that one could not build up an industry on such a small quantity. The same was true of the uranium catalyst suggested by Haber. Not recalling that iron had been used before, Bosch suggested that experiments be made with it, supporting his suggestion with the remarkable reason that iron shows a complicated spectrum. The iron had to be produced directly from iron ore by reduction at comparatively low temperatures. Many experiments were carried out by Mittasch, of which a great many were negative, some satisfactory, and only a few showed good results. The best results were obtained with a Scandinavian iron ore, which was carefully analyzed. A considerable amount of alumina was found in it. Experiments proved the importance of admixture of alumina. Thus the so-called mixed catalysts, which afterwards played such an important part, were discovered. When Mittasch later on found time to occupy himself more intensively with the history of the catalysis, he and his collaborator, Theis, discovered that former scientists, especially Doebereiner, Magnus, Wöhler, Fand Mahla, and Deacon knew of the existence and importance of mixed catalysts, but that the knowledge of this group of substances had been completely lost.

Despite this fundamental research in the field of ammonia synthesis from its elements, Haber was not contented. He studied the so-called cold luminous arc and found that the formation of nitric oxide can be brought to high concentrations if sufficient ionization energy is added to the system. It may be assumed that this research work would have had important technical consequences if Haber had not invented and perfected the synthesis of ammonia from the elements which could be made on the greatest technical scale.

Before and during these important investigations Haber carried out other exceedingly valuable researches, partly in the field of gas chemistry, the coal element and the hydrogen-oxygen element. Haber recognized the Jaques coal element which was heralded widely to be a hydrogen-oxygen element. He destroyed the hopes which had been put in the direct electrochemical transformation of the coal energy into electric power. Furthermore, research was carried on in the following fields: beryllium compounds, production of aluminum, water gas equilibrium in the Bunsen flame, the theory of the speed of reaction in heterogeneous system, the principles of the separation of gases by centrifugal force, the anodic attack of iron by tram streams in the earth, the passivity of iron and the formation of surface layers, the reversible action of oxygen upon magnesium chloride and electric interfacial forces. One result of these important investigations is the glass electrode which has proved so valuable for pH measurements. Many of these investigations have become starting points for new research work.

All this important and basic research did not exhaust Haber's working power. He occupied himself with investigations regarding the escape of electrons from metals when they are transformed in oxides or salts. This research work was an important incentive for photochemical investigations carried out later on. Before the War he published important data on the optical analysis of gas mixtures and the development of the gas interferometer which carries his name and that of Dr. Löwe. Furthermore, papers were published on investigations regarding acoustic analysis of gases and the construction of the firedamp whistle. The latter contributions, especially the one on optical analysis of industrial gases, have become exceedingly valuable. Haber's conception of adsorption, which he attributed to the effect of radiating incompletely saturated attractive forces of the atoms in the space lattice, was of great consequence to further scientific research. According to his theory, molecular forces may be looked upon as being the effects of chemical valence forces, or, in other words, the effect of electromotive forces.

An important period in Haber's life was the World War. The writer knows from Haber's own lips how much he detested war and the horrors connected therewith. However, when this catastrophe occurred, Haber placed his services completely at the disposal of his people whose government, nineteen years later, rewarded him with base ingratitude. Haber was of the opinion, which is certainly correct, that the scientist in times of peace belongs to the world, but in times of war to his country. As early as November, 1914, the writer, who at that time was chief chemist of the Austrian War Ministry, came in contact with Haber. The Central Powers realized soon after the beginning of the War that the conflict would last much longer than Christmas, 1914, and that one had to prepare for a longer period. First it was necessary to produce great quantities of nitric acid—more than ninety-five per cent. of the total gun powder and explosives were based on nitric acid. It may be mentioned here that the Central Powers were not prepared for war. No measures had been taken to substitute nitrogen-oxygen compounds for Chile saltpeter, which was used exclusively at that time by the Central Powers. A small ammonia combustion plant was located in Gerthe near Bochum, Germany, and a still smaller air combustion plant was in Patsch near Innsbruck, Austria. Haber's first efforts were directed toward supplementing the amount of ammonia which could be obtained from coke oven plants. This was accomplished by increasing the production with the Haber-Bosch process and of calcium cyanamide. Ammonia obtained in this manner had to be transformed into nitric acid in ammonia combustion plants. The diluted acid had to be highly concentrated or converted into artificial saltpeter. To accomplish this required more than one year. The small amounts of saltpeter which were present in Germany and in Austria at the beginning of the War would certainly not have been sufficient to meet the demand. It may not be generally known that after the fall of Antwerp, fifty thousand tons of Chile saltpeter

were found in the storehouses along the harbor which became accessible to the Central Powers. If this supply of Chile saltpeter had not been there, or if it had been thrown into the River Schelde, the War, in the opinion of the writer, would have ended not later than Spring, 1915, on account of lack of explosives.

The second great achievement of Haber, who was frequently to be found in the front trenches, was in the organization of the gas war. Haber, later on, was reproached a great deal for it. However, if one accepts war as such, these reproaches certainly were not justified. It is beyond dispute that gas explosives, even though rather ineffective, were first used by the French army. Haber directed the measures for the chlorine gas attack which were temporarily successful at Ypres in the spring of 1915. Inasmuch as one had to depend on the direction and change of wind, the blow method was substituted later on with gas shells. Haber prepared not only for the offensive, but also for the defensive. Under his direction fundamental research work on gas mask protection was carried on. Gas masks, as well as gas war substances, have proven very valuable after the War, the latter especially for the destruction of vermin. From this it may be seen that what was originally planned for destruction turned out to be a blessing in the end.

After the War, Haber returned again to his beloved science—always with the thought to mitigate as much as possible the consequences of the War. It is known that he made thorough studies to determine if the enormous quantities of gold present in the oceans might not be recovered to pay Germany's war debt. After several years of intensive work, however, he had to discontinue this plan, since due to insufficient concentrations, the recovery of the gold in sea water would have been too expensive.

As early as before the War, Haber took over the direction of the Kaiser Wilhelm Institut for Physical Chemistry, which he made famous. Everybody knows that this institution attained world fame under his direction and through the excellent collaborators who gathered around him.

After the War, Haber broadened the base of his activities. He published important scientific articles regarding the most diversified fields. Above all this, he placed his services more and more at the disposal of his people. While before and during the War he published articles on investigations of ammonia equilibrium at normal and increased pressures and the determination of the heat formation of ammonia from its elements at different temperatures, after the War he carried out important research work on amorphous precipitations and crystallizing soles which resulted in the determination of the coalescence velocity and the rearrangement velocity. Combined with his research work regarding the presence of gold in sea water are his investigations on the production of artificial gold from mercury. The contributions of Miethe and Stammreich, which created a sensation, could not be disregarded, as it seemed possible that mercury with the atomic number 80 could be transformed into gold with the atomic number 79 by the splitting off of one electron. However, when besides gold, silver with the atomic number 47 could be detected in considerable quantities, it was clear that gold and silver were mere contaminations contained in the mercury used in other parts of the apparatus. This fact has been completely confirmed later on.

Among his last exceedingly important researches with his collaborators, the one on the mechanism of combustion and the radicals found in flames is especially remarkable. With Bonhoeffer he examined flames spectroscopically and found active hydrogen, hydroxyl, dicarbon, and methene. The conception of the chain reaction by Bodenstein in 1912–13 gave Haber the key to the explanation of the reaction in flames. The last years of his scientific work were devoted to the chain reactions. With Franck he recognized that the autoxidation of watery sulfite solutions represents a chain reaction started either by cupric ions, ultra-violet radiation, or oxidizing agents, whereby the radical SO_3 or monothionic acid, SO_3H, continues the reaction. Of fundamental importance are the investigations published with Willstätter on radicals in the chain-reaction mechanism of organic and enzymic processes. This permitted the classification of a large number of reactions under one heading. The contact substances (enzymic or ferric compounds) are reduced monovalently. The substratum in the starting reaction is oxidized monovalently. In the main reactions the dehydrogenation product—a radical—is formed which would indicate a valence loss with carbon, less frequently with oxygen. From this radical I another radical II is formed, aside from the end-product determined by the other reagents present. The monodesoxy enzyme or the ferro compound formed from the enzymic or the ferri compound is oxidized by oxygen or another oxidizing agent with or without the help of the substratum. Through repetition the main reactions I and II produce this chain which ends only if two similar or two dissimilar radicals disappear. Another way of breaking the chain is through the interaction of a radical with an inhibitor.

The catalysis of hydrogen peroxide through ferrous compounds is explained by the following chain reaction:

$$\begin{aligned} Fe^{II} + H_2O_2 &= Fe^{III}(OH) + OH \\ OH + H_2O_2 &= H_2O + O_2H \\ O_2H + H_2O_2 &= O_2 + H_2O + OH \\ Fe^{II} + OH &= Fe^{III}(OH) \end{aligned}$$

It cannot be foreseen what further consequence these last researches will have in the field of flames, explosions, synthesis, and enzymes.

Haber's activities did not end, however, with the accomplishment of great scientific research. After the War, when the pursuit of scientific studies seemed to languish in Germany because of inflation and other matters, it was he who created the "Notgemeinschaft der Deutschen Wissenschaft." This institution was exemplary and most beneficial. Advised by representatives of science and industry, a board of trustees functioned which supplied scientists with the means for carrying out research work on a large scale. This money

was supplied by the State. Valuable apparatus could be bought which, after having served at a certain place, was sent to other places where it was needed.

In the Kaiser Wilhelm Gesellschaft Haber's influence was of greatest importance. This Society established a great number of research institutes, of which the Kaiser Wilhelm Institut for Physical Chemistry was the first. The first president of the Kaiser Wilhelm Gesellschaft was the famous theologian Harnack, the grandson of Justus Liebig. The second president was Max Plank. When Harnack was asked what he did to make this organization famous, he answered, "I chose the most brilliant scholar in his field, and the Kaiser Wilhelm Gesellschaft built the Institute around him."

Haber was among the first who were successful in reëstablishing relations broken during the War with scientists of other countries. He deserves great credit for this. Just as he did his best during the War for the common good of his people, so after the War he was the first to recognize the international position of science and its representatives and made all efforts to tear down hampering barriers.

Haber was one of those few men in whom scientific creative power was united with wonderful ethical qualities. Anyone who came in contact with him was richer for it—he always gave, while the other received. The latter years of his life were sometimes aggravated by sickness, from which he partially recovered. His prophetic words spoken six years before his death and dedicated to Liebig, hold good for him.

"And now he goes, filled with the thought and action of chemistry as its champion and hero, with slower-moving steps to the end of his life."

Haber was endowed with a great intellect. He was able to separate almost instantaneously and with unprecedented sagacity the essential and valuable from unimportant matters. He was a master of the written word. His treatises are distinguished by their clearness of description. His lectures are master works. His last academic lecture was given on request of the writer on the occasion of the Liebig-Wöhler celebration in Darmstadt in 1928. The real Haber certainly cannot be defined better than by his own words in which he portrayed Liebig in this wonderful lecture, and which really might be called Haber's autobiography.

"We ask, before we take leave of him, after having said so much of his strength of will and mind, how was it with his soul? For no one deserves to be counted among the immortals—no matter how great his power, and inspired his mind—if he lacks greatness of soul. All who knew him say of him that he was true from the bottom of his heart, upright and good, yet proud and of high thoughts. . . . Friends tell of events which show that he was kind-hearted and helpful. But it seems to me that more than such characteristics of a man is the love which he has gained and which follows him beyond the grave. I know of none among the warriors of our science, yea in the whole field of natural science, who received more grateful love during his life and who had greater love follow him into eternity."

CHEMICAL POLICEMEN

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CHEMICAL reactions, like social processes, require regulation for orderly activity. The guardians of our society are but a handful in the vast aggregate. The guardians of chemical reactions constitute a very small part of the total reaction mixture. In this paper we propose to study the activities of some chemical policemen. We shall observe how the chemical policemen speed up some reactions, halt others, and by their directive influences make many commercial processes realities instead of test-tube dreams.

Gasoline.—Many of us can appreciate the value of that minute dash of lead tetraethyl in gasoline which retards the explosion in the cylinder, eliminates the objectionable knock, and forces the gasoline to deliver smooth power. How much value would that gasoline possess if, in the short time between manufacture and comsumption, the gasoline became yellow, cloudy, and gummy? Today cracked gasoline, with an increasing market due to low price and high power, and certain natural gasolines contain large percentages of unsaturated compounds. These unsaturates, in the presence of atmospheric oxygen or peroxides rapidly polymerize to sticky, objectionable gums. This polymerization is controlled through addition of small quantities of materials, which have the power of stopping the polymerization and thus preserving the desirable qualities of the gasoline.

Many chemical policemen can be and are used for the defence of gasoline from the depredations of oxygen. They include hardwood tar fractions (*1*), aminophenols (*2*), acylaminophenols (*3*), polyhydroxyaromatics (*4*), alpha-naphthol and alpha-naphthylamine (*5*), aryl or arylalkyl aminophenols (*6*), and closely allied products. These compounds are all antioxidants and, indeed, a correlation has been established between gum inhibitory power and critical oxidation potential (*7*).

Gasoline needs not only an anti-gum squad, but also color preservatives. Color protection is achieved through the use of a chemical policeman from the group

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of alkanolamines, urea, the less volatile amines, and complex ring systems like naphthalene, phenanthrene, acenaphthene, anthracene, and fluorene. Further studies are in progress (*8*).

Rubber.— Only a few years ago the rubber tire was an ephemeral part of an automobile. Car owners were stretching the truth (to the delight of the manufacturers) when they claimed mileage lives of 5000 and 6000 for their tires. Now reasonably priced tires last four and five times this distance. This remarkable result has been achieved through recognition of sunlight and oxygen as rubber's worst enemies. Modern chemical policemen so retard oxidation by air and checking by sunlight and dry flexing that rubber products live to a ripe old age, instead of dying of rapid degeneration in their youth.

Illustrative of the rubber policemen are the following: guanidine and its derivatives (*9*), alkali and alkaline earth salts of α-nitroso-β-naphthol (*10*), the reaction product of glycine and benzaldehyde (*11*), nitrosophenols, aldehyde-amine condensation products including Schiff's bases (*12*), phenyl-β-naphthylamine and other diaryl secondary amines (*13*), the reaction product of carbon bisulfide and aryl orthodiamines (*14*), the reaction product of aliphatic amines and hydroxy derivatives of benzene (*15*), asphaltic derivatives of petroleum distillates produced by hot air blowing (*16*), tri-*o*-cresyl phosphate and esters of aromatic sulfonic acids (*17*), aldol naphthylamines (*18*), and aliphatic amino acids (*19*).

The process of vulcanization, even many years after its discovery by Goodyear, was a lengthy one. Nowadays vulcanization is accomplished in a hundredth of the time by incorporating vulcanization accelerators in the rubber mix. The following classes of compounds are illustrative of these hurry-up policemen (*20*): guanidine and its derivatives, aldehyde ammonias and anilines, dithiocarbamides, xanthates, thiurams, and mercaptobenzothiazoles. It is at once apparent that many substances combine the function of antioxidant with that of accelerator.

Among the foregoing compounds are a few that deserve special mention. These are the ultra-accelerators. By a judicious use of one of this class of compounds a reaction can be completed virtually with the mixing of the reagents. We might mention pentamethylene dithiocarbamate of piperidine, $(C_5H_{11}.C_5H_{11}N)^+(S.CS.NH_2)^-$, *sym*-tetramethyl thiuram, $(CH_3)_2.N.CS.S.CS.N.(CH_3)_2$, and cyclohexyl ethylamino dithiocarbamate, $(C_6H_{11}.NH_2.C_2H_5)^+(S.CS.NH_2)^-$. These accelerators are so effective that vulcanization must be retarded lest the rubber mixture cure before it can be molded. As retarders we find policemen in thermolabile combination with the accelerator. In common use are zinc chloride, substituted benzoic acids, and thermally unstable salts of the accelerators with mineral acids.

Food Preservation.—It is well known that food can be preserved from invading microörganisms by the use of preservatives, albeit at the cost of some eventual damage to the ultimate macroconsumer. For example, sodium benzoate was long employed as a food preservative, although its popularity is waning with the growing rigor of pure food law enforcement.

We are only beginning to check the omnipresent onslaught of the oxygen in which we live. Certain medicinals, notably the fish oils of high vitamin potency, are now being guarded by the use of small quantities of antioxidants. A very minute amount (0.005 per cent.) of hydroquinone is commonly used to prevent rancidity. Musher (in a long series of patents 1934 to 1936) has claimed that freshly ground cereal surfaces will protect oxidizable foods from the early onset of oxidation. The methods outlined above are being rapidly extended.

Rust Removal and Prevention.—The removal of rusty scale from iron and steel is one of the major problems in their fabrication (*21*). One cheap obvious way to remove rust is to "dissolve" it with mineral acid, but acids have an avid taste for the metal. The problem, then, was to confine the acid to a diet of rust without an attack on the metal. Another class of chemical policemen was called in, the pickling inhibitors. (Technically, the process of scale removal is called pickling.) These inhibitors are genuine catalysts in the sense that an extremely minute quantity of them is required to inactivate the acid toward the metal. The most effective inhibitors are basic derivatives of acridine (*21*). An interesting application of this use of inhibited acids is that with their aid it is now possible to rejuvenate oil wells which have ceased to produce normally. The method of rejuvenation consists of pumping inhibited hydrochloric acid through the iron pipes and well fittings down into the underlying limestone formations. There the acid attacks the stone; the resultant carbon dioxide replaces the exhausted natural gas in its function of forcing up oil. At the same time the oil in the pores of the rock becomes available. This is one of the two standard ways of "repressuring" an exhausted oil well. Since the entire operation is necessarily carried on in and through the iron pipes of the well, the procedure is manifestly impossible without the use of the chemical police.

Other recent developments in the protection of metallic surfaces by chemical means are no less interesting than the pickling inhibitors. Very small quantities of pentavalent arsenic in fifty per cent. phosphoric acid will prevent the acid from attacking the walls of the steel cars in which it is shipped (*22*). Using sea ooze in special paints (*23*) results in rust protection apart from the protection furnished by the paint. Tannin in locomotive boiler water (*24*) retards corrosion of the vital surfaces of the iron horse. An interesting sidelight is that the tannin is only effective at boiler temperatures.

Lubricants and Lubrication.—Lubricants play a vital part in our modern life. Certain of the army of chemical policemen play a vital rôle in the life of modern lubricants. Harmful wax which keeps oil from flowing at low temperatures is checkmated by the chemical policemen that forestall its crystallization. For

instance, the addition of small quantities of the condensation product of long chain paraffins with aryl compounds via the Friedel-Crafts reaction (*25*) will lower the pour point of petroleum products. A similar result is obtained by use of alkyl polysubstituted five and six membered rings with oxygen substituents (*26*).

With the advent of modern high-speed machinery, engineers were forced to design new gear shapes for quiet, efficient operation. Some of these gears, like the hypoid, develop tremendous pressures at the bearing surfaces. Ordinary lubricants are squeezed out between such surfaces, so that a bare metal to metal contact is established and gear life is much abbreviated.

There are many theories for extreme pressure lubrication; the question is far from settled. One theory assumes that a mild corrosion of the bearing surface will help the oil remain in place and keep the bearing from seizing. Chemical policemen, like ferric chloride, are incorporated in lubricants. Another theory assumes that certain classes of compounds are strongly adsorbed by metal surfaces and thus function as border line lubricants. Hence, long chain fatty acids are incorporated in lubricants—the so-called "germ process" lubricants (*27*). And still others, without exhausting the list, use small quantities of compounds of phosphorus and arsenic, *e. g.*, castor oil plus a phosphoric ester (*28*).

Driers.—Another group of chemical policemen which accelerate chemical processes are the compounds used as paint driers.

Let us consider first what is meant by the drying of paint. Paint consists essentially of a pigment suspended in an oily vehicle.* The pigment, after the paint has dried, must be held tenaciously in a film; otherwise the pigment will powder off like sand from sandstone. Were the vehicle to evaporate, there would be nothing to keep the pigment on the painted surface. Obviously the drying of paint is not drying in the ordinary sense of the word where the vehicle is dispersed into the surrounding phase. As a matter of fact the drying of paint is not drying at all (except as thinner is lost); it is an oxidation.

Linseed oil, or some other drying oil like tung, oitica, or fish oil, is the vehicle in all paints. Compare this with lacquers where the vehicle is a film of a plasticized cellulose derivative, and the drying is due to the evaporation of a solvent.

An important constituent of linseed oil is glyceryl trilinoleate. The latter, by a process akin to vulcanization, is air-oxidized to give a gummy viscous product. Like vulcanization, the process can be accelerated or retarded. We call the oxidation drying, and the accelerators are, therefore, called driers.

The compounds of cobalt, manganese, lead, iron, molybdenum, tungsten, chromium, tin, and nickel are recorded in the literature (*29*, *30*) as driers. Elm (*31*) has briefly summarized the requirements of a good drier as: (1) the metal must occur in two stages of oxidation and possess accelerating power; (2) the metal must be available (*i. e.*, not chemically bound in some complex); (3) the linoleate, oleate, margarate, or some other oil-soluble derivative of the metal must be used. This is because the vehicle and the thinners are oily, and an insoluble drier is just so much sand for drying ability. The common driers are the lead, cobalt, and manganese salts of the unsaturated acids found in natural oils. These are the C_{18} acids with one or two double bonds in the hydrocarbon chain. Besides these, there are the resinates and the naphthenates of the metals mentioned above. The latter are obtained by the hot-air oxidation of resin or naphthenic compound in the presence of an oxide of the metal whose salt is desired. The filtrate from the naphtha extraction of the oxidation product is then assayed for potency and made up to standard strength for inclusion in paint formulas.

The question of how much chemical policeman to include is settled by the nature of the paint. If a poorly drying vehicle is used, more drier is used; a fast drying oil calls for the use of less drier. If the pigment has drying qualities (iron oxide, lead oxide) less drier is added. The range of concentration (based on the total formula and calculated as active catalyst) is from 0.05 per cent. to 0.5 per cent.

* It is not to be understood that this is all that goes into good paint, but for our purposes it will be sufficient to consider only these two constituents.

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An ELEMENTARY CONSIDERATION *of* SOME NUCLEAR PHENOMENA

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INTRODUCTION

THE steady stream of new theoretical formulas and experimental data relating to nuclear physics (or chemistry) has swollen to flood stage since the discovery of artificial radioactivity by I. Joliot-Curie and F. Joliot in 1934 (*1*). During the forty years of persistent investigation since the discovery of natural radioactivity, there have been clearly distinguished about forty instances involving the emission of either alpha or beta particles. In contrast, in the two years since the announcement of artificial or induced radioactivity not less than fifty individual instances have been reported. These involve the emission of particles which, for the most part, are electrons or positrons, rarely alpha particles.

Within the past decade the number of commonly recognized elementary particles has been increased from two, the electron and the proton universally recognized for a quarter of a century, to include half a dozen new, more or less clearly defined, units. The situation in this respect is summarized in the following table of elementary or fundamental particles (Table 1).

For the average student interested in atomic structure much of the frequently contradictory data is confusing and ofttimes misleading. Although the only sure way out of this predicament lies in still more extensive and precise experimentation and clearer interpretation of the data on theoretical grounds, it does seem possible at the present time to draw a few generalizations which may afford a clearer conception of nuclear phenomena. The purpose of this paper is to present a non-mathematical view of the nuclear transformations and artificial radioactivity of the lighter elements. No attempt is made to consider such features as spin concepts, nuclear energy levels or momentum factors so that a certain amount of absolute accuracy has necessarily been sacrificed.

BASIC THEORY

The entire presentation may be considered to rest on two fundamental laws, namely:

1. the law of conservation of mass-energy,
2. the law of conservation of electric charge.

The phrase, mass-energy, is an expression designed to include in one term both the energy as ordinarily conceived and the energy thought of as somehow bound together to yield the mass associated with a particle. The first law involves the application of the well-known Einstein equation

$$E = mc^2, \tag{1}$$

where c is the velocity of light and E the increase (or decrease) in energy resulting from the destruction (or creation) of the mass, m. The second law merely implies that in any reaction the sum of all the positive and negative charges must equal zero.

As a preliminary illustration of this interchange between mass and energy, let us consider the case of two particles such as an electron and a positron coa-

TABLE 1

IMPORTANT PARTICLES IN ATOMIC STRUCTURE

Name	*Symbol*	*M*	*Q*	*Occurrence*
Electron (Negatron)	e	H/1850	−1e	Probably exists as an entity in the external parts of all atoms. Appears from the nuclei of atoms on bombardment by cosmic or gamma rays and from the nuclei of radio-elements.
Positron		H/1850	+1e	Appears from the nuclei of atoms on bombardment by cosmic or gamma rays and from the nuclei of artificial radio-elements.
Neutrino	..	<H/3700	0	Postulated on theoretical grounds to accompany beta rays, but no conclusive experimental evidence for its existence yet presented.
Proton	p	1H	+1e	Nucleus of the light hydrogen atom. Probably exists as an entity in the nuclei of all atoms.
Neutron	n	1H	0	Probably exists as an entity in the nuclei of all atoms except light hydrogen.
.....*	..	(1H)	−1e	Postulated on theoretical grounds to exist in the nuclei of heavy atoms, but no conclusive experimental evidence for its existence yet presented.
Deuteron	d	2H	+1e	Nucleus of heavy hydrogen (deuterium). Probably a combined proton and neutron. Possibly exists as an entity in the nuclei of all atoms except light hydrogen.
Alpha Particle	α	4H	+2e	Nucleus of helium atom. Appears from nuclei of radio-elements and probably exists as an entity in the nuclei of all atoms except the hydrogens and light helium. Probably a combination of two protons and two neutrons or of two deuterons.
Photon	..	$h\nu/c^2$	0	Quantum of radiation.

M, approximate mass of the particle in terms of the mass of a hydrogen atom, H.
Q, charge on the particle in terms of the charge on the electron.
h, Planck's constant; *c*, velocity of light; ν, frequency of radiation.

* The word "Notron" is proposed as a name for this particle.

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lescing so as to destroy each other with the emission of energy as a gamma ray. Assume for purposes of illustration that the rest masses of both the electron and the positron are the same and equal to 9×10^{-28} g. and that the speed of light is 3×10^{10} cm./sec., then applying Equation (1) gives

$$2 \times 9 \times 10^{-28}\text{ g.} \times (3 \times 10^{10}\text{ cm./sec.})^2 = 162 \times 10^{-8}\text{ ergs}, \\ = 162 \times 10^{-15}\text{ joules},$$

for the energy of the emitted gamma ray. This value could of course be expressed in terms of any energy units, *e. g.*, calories, but it has become customary to express nuclear energies in terms of million electron-volts, (MEV). To express the above energy in terms of MEV, use may be made of the equation $E = Ve$, where V is the potential gradient and e is the charge on the electron (1.591×10^{-19} coulombs).

$$\text{Therefore } V = 162 \times 10^{-15}\text{ joules}/1.591 \times 10^{-19}\text{ coulombs}, \\ = 1.02 \times 10^{6}\text{ joules/coulomb (}i.\ e.\text{, volts)},$$

and the energy is 1.02 MEV.

We have here considered the hypothetical case of the conversion of an electron-positron pair into a gamma ray. The reverse process has been observed experimentally in cosmic ray phenomena and in fact led to the discovery of the positron (*2*). The energy value obtained above is therefore interpreted to mean that a gamma ray having the energy equivalent of slightly more than 1 MEV, may under the proper conditions convert itself into an electron-positron pair. If the gamma ray energy is considerably greater than 1 MEV the excess will manifest itself as extra kinetic energy, ejecting the electron and positron with definite velocities.

By a similar calculation* the mass equivalent of 1 MEV, *i. e.*, E/c^2, may be shown to be 1.591×10^{-6} ergs/$(3 \times 10^{10}$ cm./sec.$)^2 = 17.70 \times 10^{-28}$ g., which, in terms of atomic mass units (AMU), becomes 0.001074 AMU. The value 0.001074 AMU/MEV is an important conversion factor in nuclear reactions.

NUCLEAR REACTIONS

As is well known, nuclear reactions necessarily involve changes in atomic mass and/or atomic number and are produced artificially as the result of bombarding a target with suitable projectiles, *e. g.*, protons, neutrons, deuterons, alpha particles and gamma ray photons. Two general types of such artificial nuclear reactions may be distinguished: first, those resulting in the formation of stable elements, and second, those resulting in the formation of unstable or radioactive elements, the so-called radio-elements. These radio-elements, like the naturally radioactive substances, spontaneously disintegrate at a rate characterized by their half life.

Formation of Stable Elements

An example of this type of reaction is the thoroughly investigated case in which lithium has been bombarded with protons resulting in the production of alpha particles. This reaction may be represented symbolically as

$$_3\text{Li}^7 + {}_1\text{H}^1 \longrightarrow 2\,{}_2\text{He}^4 + E. \qquad (2)$$

The subscripts and superscripts applied to the symbols for the chemical elements represent respectively the atomic number and mass number. The mass number of any element represents the closest integer to the isotopic atomic mass and in all cases differs numerically from the atomic mass by less than 0.02 AMU. The equation should perhaps more properly be written

$$_3\text{Li}^7 + \text{p} + E_p \longrightarrow 2\alpha + 3e_0 + E_\alpha,$$

where E_p is the kinetic energy of the bombarding proton and E_α is the total kinetic energy of the resulting alpha particles, so that $E_\alpha - E_p = E$. Consequently, E may be considered as the energy resulting from the reaction due to a difference in mass between the initial and final products. The electrons e_0 are extra-nuclear or orbital electrons and involve no significant energy changes. The alternative form, which is in accordance with common practice, has therefore been used to avoid confusion involved in introducing the orbital electrons necessitated by the second law.

The energy, E, may be determined experimentally by examination of the tracks exhibited by the protons and the recoil alpha particles in a Wilson cloud chamber. In this fashion E has been determined experimentally (*3*) as 17.06 MEV, which, by the application of Equation (1), may be expressed as 0.0183 AMU. Obviously, E may also be evaluated by the application of mass spectrographic data to Equation (2). Thus applying the appropriate atomic masses listed in Table 2 gives

$$E = [7.0176 + 1.0081 - 2(4.0039)]\text{AMU} = 0.0179\text{ AMU},$$

which is in good agreement with the experimental value obtained from disintegration data.

The reaction just considered results in the liberation of energy. A familiar example of a reaction in which energy is absorbed is one involving the bombardment of deuterium by gamma rays. This reaction may be expressed as

$$(h\nu)_\gamma + {}_1\text{H}^2 \longrightarrow {}_1\text{H}^1 + {}_0\text{n}^1. \qquad (3)$$

Substitution of the appropriate atomic masses in this equation gives

$$(h\nu)_\gamma = (2.0147 - 1.0081 - 1.0089)\text{AMU} = -0.0023\text{ AMU}.$$

This energy may be expressed as 2.14 MEV and interpreted as the minimum energy ($h\nu$) a gamma ray must have in order to "split" the deuterium atom. The experimental value (*4*) of E is reported as -2.26 MEV, *i. e.*, -0.0024 AMU.

The following reactions, for all of which energy values have been obtained from experimental data,

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* 1 MEV = 10^6 volts $\times$ 1.591×10^{-19} coulombs $\times$ 10^7 ergs/joule = 1.591×10^{-6} ergs.
1 MEV = 1.591×10^{-6} ergs/4.18×10^7 ergs/calorie = 3.81×10^{-14} calories.
1 AMU = $1/16$ mass of $_8\text{O}^{16}$ atom or
1 AMU = mass of hydrogen atom/atomic mass of hydrogen or
1 AMU = 1.662×10^{-24} g./1.008 = 1.648×10^{-24} g.

In order to obtain another concept of the magnitude of the energies involved, it may be noted that the energy liberated during the combustion of carbon is about four electron-volts per molecule of carbon dioxide formed.

reveal something of the variety of possible transformations resulting in the formation of stable elements.†

$$_4Be^8 + {}_0n^1 \longrightarrow {}_4Be^9 + 1.5 \text{ MEV}$$
$$_4Be^9 + {}_1H^1 \longrightarrow {}_5B^{10} + 6. \text{ MEV}$$
$$_5B^{10} + {}_0n^1 \longrightarrow {}_3Li^7 + {}_2He^4 + 1.95 \text{ MEV}$$
$$_7N^{14} + {}_0n^1 \longrightarrow {}_3Li^7 + 2{}_2He^4 - 7.0 \text{ MEV}$$
$$_3Li^6 + {}_1H^1 \longrightarrow {}_2He^4 + {}_2He^3 + 3.6 \text{ MEV}$$
$$_4Be^9 + {}_1H^2 \longrightarrow {}_5B^{10} + {}_0n^1 + 4.93 \text{ MEV}$$
$$_3Li^6 + {}_1H^2 \longrightarrow {}_3Li^7 + {}_1H^1 + 5.0 \text{ MEV}$$
$$_8O^{16} + {}_1H^2 \longrightarrow {}_7N^{14} + {}_2He^4 + 2.95 \text{ MEV}$$
$$_3Li^7 + {}_2He^4 \longrightarrow {}_5B^{10} + {}_0n^1 - 3.0 \text{ MEV}$$
$$_{13}Al^{27} + {}_2He^4 \longrightarrow {}_{14}Si^{30} + {}_1H^1 + 2.07 \text{ MEV}$$

Obviously the mass-energy data derived from such transmutation reactions may be used to establish another method for the determination of the atomic masses of the elements. While the normally occurring isotopic mixture of oxygen (O = 16.0000) has been adopted as the standard of the chemical system of atomic masses, the isotope of oxygen ($_8O^{16}$ = 16.0000) has been adopted as the basis for the system of isotopic atomic masses. Whenever possible, it is, therefore, desirable to compare the masses of other atoms directly to that of the most common oxygen isotope. Such a direct comparison is particularly desirable for those elements whose nuclei are commonly utilized as bombarding agents in nuclear reactions. Aston, Bainbridge, and others using the mass spectographic method have quite accurately determined the atomic mass of helium referred directly to that of oxygen and in turn the atomic masses of hydrogen and deuterium referred directly to that of helium. The atomic mass of helium, therefore, becomes an important secondary standard. The following set of five reactions obtained from the excellent work of Cockcroft and Lewis (*5*) illustrates the application of the mass-energy method to obtain another more or less direct comparison between the atomic masses of helium and oxygen.

$$_8O^{16} + {}_1H^2 \longrightarrow {}_7N^{14} + {}_2He^4 + 2.95 \text{ MEV}$$
$$_7N^{14} + {}_1H^2 \longrightarrow {}_6C^{12} + {}_2He^4 + 13.22 \text{ MEV}$$
$$_6C^{12} + {}_1H^2 \longrightarrow {}_6C^{13} + {}_1H^1 + 2.66 \text{ MEV}$$
$$_6C^{13} + {}_1H^2 \longrightarrow {}_5B^{11} + {}_2He^4 + 5.11 \text{ MEV}$$
$$_5B^{11} + {}_1H^1 \longrightarrow 3\,{}_2He^4 + 8.8 \text{ MEV}$$

When these five equations are added all the particle terms, except $_8O^{16}$, $_2He^4$, and $_1H^2$ cancel and the sum gives

$$_8O^{16} = 6{}_2He^4 - 4{}_1H^2 + 32.74 \text{ MEV}. \qquad (4)$$

In order to eliminate $_1H^2$ from this equation it is necessary to revert to mass spectrographic data for the best value for the ratio $_1H^2/{}_2He^4$, which, from the values given in Table 2, is found to be 0.50319. The atomic mass of helium may then be calculated to be 4.0040 AMU. However, it should be remembered that the accuracy of the determinations of the energies involved determines the accuracy of the value of the atomic mass. Since there is a slight disagreement between various workers regarding some of the energy values, there is still some disagreement as to the "true" atomic mass of helium. For example, Cockcroft and Lewis by a calculation similar to that above obtained the value 4.00377 ± 0.00017 AMU while Bethe (*6*), using a different set of reactions, obtained the value 4.00336 ± 0.00023 AMU as the "standard" atomic mass of helium. Nevertheless, the discrepancies that now exist in the various values for the atomic masses of the lighter elements amount to only a few parts in 10,000.

Use of these bombarding agents frequently results

† Many of the synthetic products of nuclear reactions are known to emit gamma rays. However, the consensus of opinion seems to be that gamma ray emission is produced during transitions from excited nuclear energy states (similar to the emission of "light" during transitions from excited electronic states), but, as was indicated earlier, this phase is intentionally omitted in this discussion.

TABLE 2

RELATIVE ISOTOPIC ABUNDANCE AND MASSES OF STABLE ELEMENTS

	Relative Isotopic Abundance	*From Mass-spectrographic Data*	*From Mass-energy Data*	*International Union of Chemistry Values*	
$_0n^2$		1.0089	1.0091		
$_1H^1$	99.97	1.00812*	1.00812*		
$_1H^2$	0.025	2.01471*	2.01471*	1.0078	$_1H$
$_1H^3$	(10^{-6})	3.0151	3.0171		
$_2He^4$	100.0	4.00391*	4.00391*	4.002	$_2He$
$_3Li^6$	8.3	6.0175	6.0167		
				6.940	$_3Li$
$_3Li^7$	91.7	7.0176	7.0180		
$_4Be^8$	0.05		8.0078		
				9.02	$_4Be$
$_4Be^9$	99.95	9.0164	9.0149		
$_5B^{10}$	20.	10.0135	10.0161		
				10.82	$_5B$
$_5B^{11}$	80.	11.0121	11.0128		
$_6C^{12}$	99.75	12.0035*	12.0036		
				12.00	$_6C$
$_6C^{13}$	0.25	13.0051	13.0073		
$_7N^{14}$	99.86	14.0042	14.0073		
				14.008	$_7N$
$_7N^{15}$	0.14	15.0032	15.0048		
$_8O^{16}$	99.81	*16.0000*	*16.0000*		
$_8O^{17}$	0.03	17.0024	17.0046	*16.0000*	$_8O$
$_8O^{18}$	0.16	18.0065			
$_9F^{19}$	100.	18.9931	19.0045	19.00	$_9F$
$_{10}Ne^{20}$	90.	19.9986	20.0021		
$_{10}Ne^{21}$	0.27			20.183	$_{10}Ne$
$_{10}Ne^{22}$	9.73	21.9947	21.9985		
$_{11}Na^{23}$	100.			22.997	$_{11}Na$
$_{12}Mg^{24}$	77.4		23.9938		
$_{12}Mg^{25}$	11.5			24.32	$_{12}Mg$
$_{12}Mg^{26}$	11.1				
$_{13}Al^{27}$	100.	26.9909	26.9909	26.97	$_{13}Al$
$_{14}Si^{28}$	89.6	27.9860			
$_{14}Si^{29}$	6.2	28.9864		28.06	$_{14}Si$
$_{14}Si^{30}$	4.2		29.9845		
$_{15}P^{31}$	100.	30.9826	30.9844	31.02	$_{15}P$
$_{16}S^{32}$	96.		31.9812		
$_{16}S^{33}$	1.			32.06	$_{16}S$
$_{16}S^{34}$	3.		33.9799		
$_{17}Cl^{35}$	76.	34.9796			
				35.457	$_{17}Cl$
$_{17}Cl^{37}$	24.	36.9777			
e 0.000547		e 0.000547	1 MEV 0.001074		

* Aston's most recent mass spectrographic values; see *Nature*, **137**, 357 (1936).

Bainbridge's most recent mass spectographic values (Reported at the Annual Meeting, American Physical Society, Atlantic City, New Jersey, December, 1936) differ slightly from Aston's values used in Table 2. These values are

$_1H^1$	1.00815	$_6C^{12}$	12.00428
$_1H^2$	2.01478	$_6C^{13}$	13.0079
$_2He^4$	4.00395	$_7N^{14}$	14.0076
$_3Li^7$	7.01822	$_7N^{15}$	15.0050
$_4Be^9$	9.01517	$_{10}Ne^{20}$	19.99917
$_5B^{10}$	10.01633	$_{10}Ne^{21}$	21.00013
$_5B^{11}$	11.01295	$_{10}Ne^{22}$	21.99870

in the formation of both stable and radio-elements* from the same parent. Two pairs of reactions involving deuteron bombardment recently reported by Fowler, Delsasso, and Lauritsen (7) and others illustrate this phenomenon beautifully. The formation of stable elements is represented as

$$_3Li^7 + {}_1H^2 \longrightarrow {}_4Be^8 + {}_0n^1 + E_1;\ E_1 = 14.3 \text{ MEV}, i.e., 0.0153 \text{ AMU} \quad (5)$$

and

$$_6C^{12} + {}_1H^2 \longrightarrow {}_6C^{13} + {}_1H^1 + E'_1;\ E'_1 = 2.7 \text{ MEV}, i.e., 0.0029 \text{ AMU} \quad (6)$$

The mechanism of the reactions may be assumed to involve the "splitting" of deuterons into protons and neutrons. A lithium atom absorbs a proton; a carbon atom absorbs a neutron. Upon this assumption an interesting mass-energy calculation may be made to determine the energy of disintegration of the deuteron. The addition of a proton to a lithium atom would produce a "heavy" mass of atomic mass (1.0081 + 7.0180) AMU, *i. e.*, 8.0261 AMU. But since the atomic mass of $_4Be^8$ is 8.0078 AMU, the mass that has been converted into energy is 0.0183 AMU. Of this the kinetic energy of the ejected neutron, E_1, accounts for 0.0153 AMU leaving 0.0030 AMU that has been converted into energy of disintegration of the deuteron. Similarly, the addition of a neutron to carbon would produce a "heavy" mass of atomic mass (12.0036 + 1.0091) AMU, *i. e.*, 13.0127 AMU and since the atomic mass of $_6C^{13}$ is 13.0073 AMU the mass that has been converted into energy is 0.0054 AMU. The kinetic energy of the ejected proton, E_1', accounts for 0.0029 AMU leaving 0.0025 AMU that has been converted into energy of disintegration of the deuteron. Both these values agree rather well not only with each other but also with the value 0.0024 AMU determined by bombardment of deuterons with gamma rays. This illustrates a common method for checking or verifying disintegration or mass-energy values.

Formation of Radio-Elements

The formation of radio-elements by deuteron bombardment of these same elements is represented as

$$_3Li^7 + {}_1H^2 \longrightarrow {}_3Li^8 + {}_1H^1 + E_2;\ E_2 = 4.3 \text{ MEV}, i.e., 0.0046 \text{ AMU} \quad (7)$$

and

$$_6C^{12} + {}_1H^2 \longrightarrow {}_7N^{13} + {}_0n^1 + E'_2;\quad E'_2 = -0.37 \text{ MEV}, i.e., 0.0004 \text{ AMU} \quad (8)$$

Since $_3Li^8$ and $_7N^{13}$ are radio-elements and are rather short lived (the half-life of $_3Li^8$ is about 0.5 seconds and of $_7N^{13}$ about 11 minutes) their atomic masses have not been determined by any of the ordinary chemical, band spectrographic, or mass spectrographic methods. However, utilizing the principle that atomic masses may be calculated from mass-energy data, the masses of the atoms of these radio-elements may be obtained as follows:

$$_3Li^8 = (7.0180 + 2.0147 - 1.0081 - 0.0046) \text{ AMU} = 8.0200 \text{ AMU} \quad (7')$$

and

$$_7N^{12} = (12.0036 + 2.0147 - 1.0091 + 0.0004) \text{ AMU} = 13.0096 \text{ AMU} \quad (8')$$

These radio-elements, $_3Li^8$ and $_7N^{13}$, disintegrate with the emission of an electron and a positron, respectively. The two radioactive disintegrations may then be represented as

$$_3Li^8 \longrightarrow {}_4Be^8 + \epsilon - e_0 + E_3;\ E^-_{max.} = 11.2 \text{ MEV}, i.e., 0.0120 \text{ AMU} \quad (9)$$

and

$$_7N^{13} \longrightarrow {}_6C^{13} + \epsilon + e_0 + E'_3;\ E^+_{max.} = 1.25 \text{ MEV}, i.e., 0.0013 \text{ AMU} \quad (10)$$

Here e_0 is an extra-nuclear electron which must be introduced into the equation to conserve mass and charge in the atomic system. The energies E_3 and E_3' are approximately equal to the energy, $E_{max.}$, with which the fastest beta rays (electrons or positrons) are emitted from the nucleus of any particular element. It is the energy $E_{max.}$ which is determined experimentally. To simplify this discussion it will be assumed† that $E_3 = E_{max.}$

Obviously Equations (9) and (10) may also be used to calculate the masses of the atoms of radio-elements. There is thus obtained

$$_3Li^8 = (8.0078 + 0.00055 - 0.00055 + 0.0120) \text{ AMU} = 8.0198 \text{ AMU} \quad (9')$$

and

$$_7N^{13} = (13.0073 + 0.00055 + 0.00055 + 0.0013) \text{ AMU} = 13.0097 \text{ AMU} \quad (10')$$

Both of these values are in good agreement with those obtained previously, Equations (7′) and (8′). The atomic masses of a number of radio-elements that have been calculated in this manner are included in Table 3.

Mechanisms

Nuclear reactions need not necessarily proceed in the precise fashion implied in the equations above, *e. g.*, by disruption on impact, and quite different mechanisms might be postulated. Thus, all successful nuclear bombardments may be considered as initially involving the capture of the bombarding particles. Such addition-products may be permanently stable, may be radioactive with measurable half-life, or may decompose so rapidly as to be regarded as disintegrat-

* The production of such elements has frequently been confirmed by direct chemical evidence as well as by spectrographic means.

† In order to account for the "continuous" velocity spectrum of the beta rays, Fermi (8) has derived a theory based on wave-mechanics in which two particles, the electron and the neutrino, are ejected from the nucleus in such a manner that the energy of the electron and the energy of the neutrino equals E_3. As a first approximation in this theory, the neutrino is assumed to have zero mass and zero charge. Fowler, Delsasso, and Lauritsen[7] have concluded from calculations on mass-energy considerations that if the neutrino has mass, its mass is less than half that of the electron. In the rest of this discussion the neutrino will play no part.

ing on impact. As a specific illustration of the latter mechanism, let us consider a reaction already discussed

TABLE 3

METHOD OF PRODUCTION AND A FEW PROPERTIES OF SOME RADIO-ELEMENTS

Method of Production (Bombarding Agent and Target)	*Radio-element*	*Half-life*	*Energy $E_{max.}$ in MEV*	*Calculated Atomic Mass of Radio-element*	*Final Stable Product*
ELECTRON EMITTERS					
d_3Li^7	$_3Li^8$	0.5 s	10.	8.0199	$_4Be^8$
d_4Be^9, α_2Li^7	$_4Be^{10}$	~10. yr	0.3*	10.0163	$_5B^{10}$
d_5B^{11}	$_5B^{12}$	0.02 s	11.	12.0154	$_6C^{12}$
d_6C^{13}, n_7N^{14}	$_6C^{14}$		1.	14.0084	$_7N^{14}$
d_7N^{15}, n_9F^{19}	$_7N^{16}$	10. s	6.	16.0066	$_8O^{16}$
n_9F^{19}	$_8O^{19}$	40. s			$_9F^{19}$
d_9F^{19}, $n_{11}Na^{23}$	$_9F^{20}$	12. s	5.	20.0076	$_{10}Ne^{20}$
$n(_{11}Na^{23}, _{12}Mg^{26})$	$_{10}Ne^{23}$	40. s			$_{11}Na^{23}$
$n(_{11}Na^{23}, _{12}Mg^{24}, _{13}Al^{27})$ $d_{11}Na^{23}$	$_{11}Na^{24}$	15. hr	1.7	23.9955	$_{12}Mg^{24}$
$n(_{12}Mg^{26}, _{13}Al^{27})$	$_{12}Mg^{27}$	10. m	0.6*		$_{13}Al^{27}$
$n(_{13}Al^{27}, _{14}Si^{28}, _{15}P^{31})$, $d_{13}Al^{27}$, $\alpha_{12}Mg^{25}$	$_{13}Al^{28}$	2.3 m	3.3	27.9895	$_{14}Si^{28}$
$n(_{14}Si^{30}, _{15}P^{31})$, $d_{14}Si^{30}$	$_{14}Si^{31}$	2.4 hr	1.85	30.9864	$_{15}P^{31}$
$n(_{16}S^{32}, _{17}Cl^{35})$, $d_{15}P^{31}$	$_{15}P^{32}$	15. d	1.7	31.9831	$_{16}S^{32}$
$n_{17}Cl^{35}$	$_{17}Cl^{36}$	50. m	2.	35.9781	$_{18}A^{36}$
POSITRON EMITTERS					
α_2Li^6	$_5B^9$	1. m	0.3	9.0163	$_4Be^9$
d_5B^{10}	$_6C^{11}$	21. m	1.3	11.0153	$_5B^{11}$
p_6C^{12}, d_6C^{12}, α_5B^{10}	$_7N^{13}$	10.3 m	1.25	13.0096	$_6C^{13}$
d_7N^{14}	$_8O^{15}$	2.1 m	1.7	15.0077	$_7N^{15}$
d_8O^{16}, α_7N^{14}	$_9F^{17}$	1.2 s	2.1	17.0080	$_8O^{17}$
α_9F^{19}	$_{11}Na^{22}$		0.4*		$_{10}Ne^{22}$
$\alpha_{12}Mg^{24}$	$_{14}Si^{27}$	14.5 m			$_{13}Al^{27}$
$\alpha_{13}Al^{27}$	$_{15}P^{30}$	3.2 m	3.	29.9888	$_{14}Si^{30}$

* — Average Energy, s—seconds, m—minutes, hr—hours, yr—years

in considerable detail, namely, the bombardment of lithium by deuterons. The initial reaction would accordingly be expressed as

$$_3Li^7 + _1H^2 \longrightarrow {}^*{}_4Be^9$$
$$7.0180 + 2.0147 = 9.0327$$

Comparison of the value of ${}^*{}_4Be^9$ with that of $_4Be^9$ given in Table 2 indicates that this addition-product possesses considerable more mass-energy. It would, therefore, be expected to disintegrate. The variety of modes of decomposition is indicated by the following partial list of possibilities.

$${}^*{}_4Be^9 \longrightarrow {}_1H^1 + {}_3Li^8 + E_1$$
$$\longrightarrow {}_0n^1 + {}_4Be^8 + E_2$$
$$\longrightarrow {}_2He^4 + {}_2He^6 + E_3$$
$$\longrightarrow {}_2He^4 + {}_2He^4 + {}_0n^1 + E_4$$
$$\longrightarrow {}_1H^3 + {}_3Li^6 + E_5$$
$$\longrightarrow {}_4Be_9 + \gamma.$$

TYPES OF REACTIONS

Tables 3 and 4 present a classification of some general types of nuclear transformations that have been observed. A close examination will reveal a number of striking parallelisms between all these reactions. For example, the products obtained on deuteron bombardment seem to follow a fairly general rule which is illustrated by Equations 5, 6, 7, and 8 and may be summarized as follows, if the parent particle of mass number $A = 2Z + 1$ (the heavier of two known isotopes of atomic number Z) ejects a proton on bombardment, then the radio-element formed is an isotope of the parent, has mass number $A = 2Z + 2$ and is an *electron* emitter, Equation (7), whereas if a neutron is ejected, a stable element of next higher atomic number is formed, Equation (5). But if the parent particle of mass number $A = 2Z$ (the lighter of two known isotopes of atomic number Z) ejects a neutron on bombardment, then the radio-element formed is an isotope of the element of next higher atomic number

TABLE 4

SOME GENERAL TYPES OF NUCLEAR TRANSFORMATIONS

Mass Number of Parent of Atomic Number Z	*Bombarding Particle*	*Particle Ejected on Bombardment*	*Mass Number of Reaction Product of Atomic Number Z'*	*Stability of Reaction Product*	*Mass Number of Final Element from Radio-element. Atomic Number Z"*
$2Z$	p	..	$2Z' - 1$	R^+	$2Z'' + 1$
	p	α	$2Z' - 1$	R^+	$2Z'' + 1$
	d	n	$2Z' - 1$	R^+	$2Z'' + 1$
	α	n	$2Z' - 1$	R^+	$2Z'' + 1$
	n	..	$2Z' + 1$	S	
	n	α	$2Z' + 1$	S	
	d	p	$2Z' + 1$	S	
	α	p	$2Z' + 1$	S	
	n	p	$2Z' + 2$	R^-	$2Z''$
	d	α	$2Z'$	R^+ or S	$2Z'' + 2$
$2Z + 1$	p	..	$2Z'$	R^+ or S	$2Z'' + 2$
	p	α	$2Z'$	R^+ or S	$2Z'' + 2$
	d	n	$2Z'$	R^+ or S	$2Z'' + 2$
	α	n	$2Z'$	R^+ or S	$2Z'' + 2$
	n	..	$2Z' + 2$	R^- or S	$2Z''$
	n	α	$2Z' + 2$	R^- or S	$2Z''$
	d	p	$2Z' + 2$	R^- or S	$2Z''$
	α	p	$2Z' + 2$	R^- or S	$2Z''$
	n	p	$2Z' + 3$	R^-	$2Z'' + 1$
	d	α	$2Z' + 1$	S	
$2Z + 2$	p	..	$2Z' + 1$	S	
	p	α	$2Z' + 1$	S	
	d	n	$2Z' + 1$	S	
	α	n	$2Z' + 1$	S	
	n	..	$2Z' + 3$	R^-	$2Z'' + 1$
	n	α	$2Z' + 3$	R^-	$2Z'' + 1$
	d	p	$2Z' + 3$	R^-	$2Z'' + 1$
	α	p	$2Z' + 3$	R^-	$2Z'' + 1$
	d	α	$2Z' + 2$	R^-	$2Z''$

R^+ designates positron emitting radio-elements and R^- designates electron emitting radio-elements. S designates "stable" elements which may, however, be produced in an excited state. In such cases the normal element of the same mass number would be formed upon the emission of a gamma ray. When two possibilities are indicated (as R^+ or S) the radio-element is formed if no stable isotope exists, *e. g.*, F, Na, Al, P have no known normal isotope of the form $A = 2Z$. In these cases the mass number in the last column applies only to the product formed from the radio-element.

There are no known stable isotopes of the lighter elements (to chlorine) having mass numbers greater than $A = 2Z + 2$.

$Z' = (Z + 1)$, has mass number $A = 2Z' - 1$ and is a *positron* emitter, Equation (8), whereas, if a proton is ejected, a stable isotope of the parent element is formed, Equation (6). Closer inspection will make evident a wide variety of more or less significant parallelisms of this kind.

Perhaps one other especially significant correlation should be indicated. A simple inspection of Column 2, Table 3, will show that radio-elements which are *electron* emitters are characterized by having mass numbers of the form $A = 2Z + 2$ or $A = 2Z + 3$ and *positron* emitters are characterized by having mass numbers of the form $A = 2Z - 1$ or $A = 2Z$. Thus, electron emitters containing Z protons and either $Z + 2$ or $Z + 3$ neutrons in the nucleus produce stable elements containing $Z + 1$ protons and either $Z + 1$ or $Z + 2$ neutrons; while positron emitters containing Z protons and either Z or $Z - 1$ neutrons in the nucleus produce stable elements containing

$Z - 1$ protons and either $Z + 1$ or Z neutrons. In the case of the electron emitters the radioactive disintegrations have been accompanied by the gain of one proton with the corresponding loss of a neutron and the ejection of an electron; while in the case of the positron emitters the radioactive disintegrations have been accompanied by the gain of one neutron with the corresponding loss of a proton and the ejection of a positron. These two exchanges may be represented in symbolic form as

$$n \longrightarrow p + e + E' \quad (11)$$

and

$$E'' + p \longrightarrow n + \epsilon \quad (12)$$

Neither of these reactions has been observed directly so that one can only speculate as to the nature of the energies E' and E'' but application of the mass-energy law implies that the reaction indicated by Equation (11) may be considered as "exothermal" by approximately 1 MEV while that of Equation (12) may be considered "endothermal" by approximately 2 MEV.

CONCLUSION

Nuclear physics and nuclear chemistry are indistinguishable. The problem of the nature of matter, common to both, has been successively narrowed from crystalline aggregates, through molecular patterns, through outer atomic architecture to inner nuclear structure, with increasing participation by the physicist. Final solution to many of the problems discussed here must necessarily await further experimental work. Once more the symbolic representation of the material chemical elements and particles may be found in the physical journals, if not on terms of equality, at least not completely overshadowed by the mathematical ψ. The application of extensive experimental work and measured data to atomic problems will doubtless be a welcome innovation to those despairing of conjuring mental concepts of wave mechanics or nominatives of the verb to undulate. It is particularly for such as these, who feel deprived of their proper birthright if barred from mechanical representation, that this paper is intended.

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THE RECOVERY OF IODINE FROM WASTE IODIDE SOLUTIONS

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DIRECTIONS have appeared from time to time(*1–17*) regarding the recovery of iodine from the waste iodide solutions which accumulate about the laboratory. Although the chemistry of these methods is well known, the technic here described may be of value because it is simple and almost quantitative in character.

FILTRATION OF WASTE IODIDE SOLUTIONS

The waste iodide solutions are usually quite acid and often contain ammonium bifluoride, used in determining copper in the presence of iron by the iodide method, which, even in dilute solutions, etches glass containers deeply over a period of several months. Therefore, great care must be exercised in handling such containers. The waste iodide solutions are decanted or filtered from any precipitated iodides. The addition of a Filter-Cel suspension to the solution permits rapid filtration. The precipitated solids are saved for further treatment. The filtrates containing the soluble iodides are placed in a large container; a small portion of the solution is reserved for later use. The iodine is recovered as follows.

REMOVAL OF THE BULK OF THE IODINE FROM THE WASTE SOLUTIONS

Precipitate the iodine in the acidified waste iodide solution by passing in chlorine gas until there is a slight

excess of chlorine present. The course of the reaction may be followed by pipetting off some of the liquid and observing whether iodine is precipitated by the addition of clear dilute potassium iodide solution. Then add enough of the reserved iodide solution to use up the excess chlorine and leave a slight excess of iodide. This point is readily recognized by a slight deepening of the color of the solution caused by the dissolving of some of the precipitated iodine. Filter on a Büchner funnel, using an ordinary filter paper previously covered with Filter-Cel laid on by filtering a Filter-Cel suspension. The filtration process is greatly facilitated by the addition of about five grams of Filter-Cel for each liter of solution. Keep the solution well stirred while filtering. Wash the iodine and accompanying filter medium at least six times, preferably more, with distilled water. In the washing process care should be taken that the surface of the iodine is not unduly exposed to atmospheric oxidation between washings, or thereafter. After washing submerge the filter paper and the precipitate in distilled water immediately. Combine the washings with the filtrate.

TESTING FOR THE QUANTITY OF IODINE STILL REMAINING AFTER THE FIRST REMOVAL

In order to determine the exact amount of chlorine water necessary to release the combined iodine as iodide in the filtrate and washings a comparative scheme of analysis is used. This method involves the titration of the free iodine initially present with a solution of sodium thiosulfate of unknown strength. Then on a separate sample all of the iodine, free or combined as iodide, is converted to iodine monochloride by the agency of strong hydrochloric acid and potassium iodate. The iodine monochloride so formed is allowed to react with potassium iodide, whereby both the iodine present as monochloride and an equivalent amount of iodine from the potassium iodide is liberated. This released iodine, after adjustment of the acidity of the solution, is then titrated with the thiosulfate solution previously mentioned. The details of the method are as follows.

A solution of KIO_3 containing about two grams per liter, and a solution of $Na_2S_2O_3$ containing about five grams per liter are prepared. The exact strength of these solutions is unimportant.

Pipet 10 to 25 cc. of the dilute iodine-iodide solution into a glass-stoppered bottle or flask. Add 5 cc. of concentrated HCL and five cubic centimeters of chloroform. Run in KIO_3 solution, shaking thoroughly after each addition, until the chloroform is just decolorized. The reactions involved are (*18*)

$$KIO_3 + 2KI + 6HCl = 3KCl + 3ICl + 3H_2O \qquad I$$

$$KIO_3 + 2I_2 + 6HCl = KCl + 5ICl + 3H_2O \qquad II$$

Add to the contents of the flask one gram of KI; after this is in solution and thoroughly mixed with the contents of the flask, add five grams of sodium acetate dissolved in 30 cc. of water, and titrate the liberated iodine with $Na_2S_2O_3$ solution until, after thorough shaking, the iodine color just disappears from the chloroform. The reactions involved are

$$ICl + KI = KCl + I_2 \qquad III$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + 2Na_2S_4O_6 \qquad IV$$

The total iodine in the solution is expressed by one-half the total number of cubic centimeters of $Na_2S_2O_3$ solution used.

Now titrate a 10- to 25-cc. portion of the dilute iodine-iodide solution with $Na_2S_2O_3$ solution, using starch solution as indicator.

Let x cc. of $Na_2S_2O_3$ be the equivalent of the free iodine in the original solution, and y cc. of $Na_2S_2O_3$ be the equivalent of iodine as KI in the original solution. Then from the equations the following relationship holds.

$$\frac{5}{4}x + \frac{3}{2}y = \frac{1}{2}\,(\text{cc. } Na_2S_2O_3 \text{ used in IV})$$

Since x is determined by titration of the free iodine in the original solution, y may be easily evaluated.

Prepare a large volume of saturated chlorine water—enough to effectively displace all the iodine in combination in the residual solution. Pipet a 10- to 25-cc. portion into an excess of KI solution. Titrate the released iodine with the $Na_2S_2O_3$ solution.

Now mix the proper volumes of chlorine water and iodide solutions. For example, suppose the iodine released by the ICL required 41.2 cc. of $Na_2S_2O_3$ solution. The free iodine in the original solution required 2.4 cc. $Na_2S_2O_3$ solution. Then

$$\frac{5}{4} \times 2.4 + \frac{3}{2}y = \frac{1}{2}\,(41.2)$$

or $y = 11.73$ cc. If the iodine released by the same volume of chlorine water requires 15.6 cc., then 11.73 cc. of chlorine water will displace the iodide iodine in 15.6 cc. of the original solution. Any oxidizing substance whose iodine displacement value can be measured in terms of the $Na_2S_2O_3$ solution may be used in place of chlorine water for this part of the recovery.

When the iodide-iodine solutions are thoroughly mixed with the proper amount of chlorine water, the resultant solution is filtered on a Büchner funnel as before, and the filtrate is treated with about five grams of activated charcoal per liter of solution or enough to remove by adsorption all the dissolved free iodine. The charcoal is then filtered on a Büchner funnel and washed well with distilled water. The charcoal and filter paper are placed in a distilling flask and enough distilled water is added to form a suspension; then a condenser is affixed and the suspension subjected to steam distillation, using auxiliary eternal heating to avoid excessive condensation in the flask, until all the iodine is driven off and condensed. The water distilled over with the iodine is again treated with a little activated charcoal to remove its iodine content and the process repeated. The final iodine solution so obtained is returned to the waste iodide container.

The final filtrate may contain traces of iodine as iodide, or a very slight excess of chlorine water. The recovery of these small amounts of iodine may be accomplished by repeating the above procedure.

TREATMENT OF INSOLUBLE IODIDES

The insoluble iodides filtered from the original solutions are treated as follows. Dissolve the precipitate in an excess of aqua regia and evaporate to dryness on a steam bath. Take up with I : I HCL and evaporate to a small bulk to remove nitric acid. Dilute and precipitate the heavy metals as sulfides with hydrogen sulfide. Filter, wash well with water, and return the filtrate to the waste iodide container for further treatment.

CONVERSION OF RECOVERED IODINE TO KI OR NAI

The conversion of the recovered iodine to potassium iodide is accomplished by combining all the filtered, thoroughly-washed iodine precipitates and suspending them in distilled water. For every 500 g. of precipitate, use about two liters of water. Pass water-washed hydrogen sulfide into this suspension until the color of the iodine disappears. Boil the solution to agglomerate the colloidal sulfur and then cool. Add at least 20 g. of activated charcoal for each 500 g. of precipitate and boil again for a few minutes. Filter on a Büchner funnel and wash well with distilled water. Exactly neutralize the clear filtrate with potassium hydroxide or potassium carbonate* and evaporate to incipient crystallization, cool, and collect the crystals. Repeat the evaporation and collection of crystals until but a small amount of mother liquor remains. Return this mother liquor to the waste iodide container.

Sodium iodide is obtained by a similar procedure; in this case the dilute hydriodic acid solution is exactly neutralized with either sodium hydroxide or sodium carbonate.

* If insufficient activated charcoal has been used there will be a black or colored precipitate at this point. Examination of this precipitate has shown it to consist mainly of sulfur. Again, if the iodine precipitates have not been thoroughly washed, the odor of ammonia may show up. In either case there is no alternative but to repeat the separation of the iodine.

TREATMENT OF SODIUM IODIDE AND OXY-IODINE WASTE SOLUTIONS

Should the original waste solutions contain iodine as sodium iodide, no variation in the indicated procedure is necessary. However, if the iodine is present as an oxy compound, KIO, KIO_3, KIO_4, it is necessary, according to the present recovery scheme, to convert the iodine in these compounds to the free state or to the iodide. This may be readily accomplished by passing sulfur dioxide into the filtered, acidified waste solutions until the color of iodine just disappears from the solution. The solution may then be treated for the removal of iodine in the manner already described.

The amount of sulfur dioxide used may be materially reduced, if, during the reduction process, the iodine is filtered off from time to time. The final dilute oxy-iodine solution is then completely reduced and subjected to the treatment with chlorine as indicated.

PURIFICATION OF IODINE

Steam distillation supplemented by auxiliary external heating offers the simplest and most convenient solution to the problem of separating the iodine from the Filter-Cel-filter-paper precipitate obtained by the present recovery method. The use of glass flasks and large diameter condenser tubes is advised; provision should be made for removing the iodine accumulating in the condenser. The iodine is filtered from the condensed water, quickly transferred to a container and dried at room temperature in a dessicator containing concentrated sulfuric acid or other appropriate drying agents.

After drying, the iodine may be sublimed. An all-glass retort, the body of which is almost totally submerged in an oil bath held at about 110°, is satisfactory. The iodine vapor is condensed in a water-cooled three liter round-bottomed flask.

SUMMARY

A simple method is presented for the recovery of iodine from waste iodide solutions.

Directions are given for the conversion of the recovered iodine into potassium iodide, sodium iodide, and for the purification of iodine.

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RECENT ADVANCES *in the* ELECTROCHEMISTRY *of* NON-AQUEOUS SOLUTIONS

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INTRODUCTION

FOR many years after the rise of the Arrhenius theory of electrolytic dissociation, investigations of the electrochemical behavior of non-aqueous solutions, with the possible exception of those in liquid ammonia, were scattered, unsystematic, and, due to experimental difficulties, often inaccurate, so that they contributed little toward the development of general solution theories. But in 1924, when Walden brought together the then available data in his masterly "Elektrochemie der Nichtwässriger Lösugen" (*1*), he was already able to call attention to the fruitfulness and promise of this field of research; and in the last twelve years the successful interpretation of certain aspects of the behavior of electrolytes by Debye and Hückel, Onsager, and others, as well as the development of the Brønsted-Lowry concept of acids and bases, has given a further impetus to the study of non-aqueous solutions. Not only has an immense amount of new data been accumulated as a result of such study, but for the first time it has become possible to discern, though as yet but indistinctly, the outline of a comprehensive theory of electrolytic solutions.

It would be quite impossible to bring a complete review of the voluminous literature on non-aqueous solutions, even for the last five years, within the scope of this article. An attempt has been made, however, first to illustrate the expansion of our knowledge of phenomena, already familiar in aqueous solution, by the study of non-aqueous analogs; secondly to present some of the new problems introduced by the divergent behavior of non-aqueous solutions; and finally to indicate the steps which have been taken toward the development of a general theory of electrolyte behavior.

CHEMICAL REACTIONS OF ELECTROLYTES

Of the many types of reactions of electrolytes which are known in aqueous solution there is scarcely any which does not have analogs in a wide variety of non-aqueous media. The most extensive studies in this field have been those in which liquid ammonia has served as solvent and dissociating medium (*2*, *3*), but many other solvents have been studied also. Metathetic reactions, especially those resulting in precipitation, have become so familiar that it is unnecessary to cite individual instances here, although it may be mentioned that fused acetamide has been added (*4*) to the list of solvents in which such reactions have been observed. Of greater interest, perhaps, is the fact that Fredenhagen and his co-workers (*5*) have found, in liquid hydrogen fluoride, a solvent in which ordinary metathetic reactions do *not* occur, although it is a good dissociating medium. The reason for this peculiarity is to be found in the extensive solvolysis which practically all salts undergo in this solvent. Fluorides dissociate as in water to yield fluoride ion, but all other salts undergo the sort of reaction illustrated by the following equations:

$$NaCl + HF = Na^+ + F^- + HCl \text{ (evolved as gas)}$$
$$KNO_3 + 2HF = K^+ + H_2NO_3^+ + 2F^-$$

Hydrogen fluoride, as these reactions show, is so extremely acid a solvent that not only are all salts solvolyzed with the formation of fluorides and free acids, but the acid so produced usually accepts an additional proton from the solvent, sometimes with the formation of a cation unknown in aqueous solution. A very wide variety of cations is capable of existing in hydrogen fluoride, but only one anion, the fluoride ion; hence, there can be no metatheses other than solvolytic reactions such as have been illustrated.

New light has been thrown on the behavior of so-called amphoteric hydroxides in alkaline aqueous solution by the study of analogous phenomena in another solvent. Zinc and cupric acetates have been found to dissolve readily in acetic acid solutions of alkali acetates (*6*), and from such solutions crystalline solvated double acetates have been obtained which are markedly similar in composition and behavior to aqueous zincates and cuprites. This fact provides confirmation for the growing belief that the latter compounds are true hydroxo salts, whose formation should be interpreted as a direct combination of amphoteric hydroxide and alkali, rather than as resulting from a hypothetical acidic dissociation of the amphoteric compound.

Acid-base titrations by both electrometric and indicator methods have been carried out in various non-aqueous media and will be referred to at greater length below. As an illustration of another important type of reaction, we may mention the experiments of Conant

and Chow (*7*), who determined the oxidation-reduction potentials of certain quinones and dyes in glacial acetic acid both by the method of mixtures and by titration of the oxidant with chromous acetate solution. These authors were also able to reduce halochromic ions of the type R_3C^+ to the corresponding free radicals, and to determine the potentials of these systems, by the use of the same reducing agent.

ELECTROLYSIS AND ELECTRODE REACTIONS; ELECTROMOTIVE FORCE MEASUREMENTS

Since 1931, when the subject of electrodeposition of metals from non-aqueous solvents was reviewed by Audrieth and Nelson (*8*), several new developments in this field have been reported. Of special interest because of its possible practical applicability is the deposition of metallic beryllium from solutions of its halides in liquid ammonia by Booth and his co-workers (*9*, *10*, *11*). Stillwell and Audrieth (*12*) describe deposits of arsenic, antimony, and bismuth obtained from acetic acid solutions of their chlorides, and Royce (*13*) mentions the deposition of platinum from solutions of platinic chloride both in acetic acid and in acetamide. Jukkola (*14*) discusses the preparation of rare earth amalgams by the electrolysis of absolute ethyl alcohol solutions of the chlorides of these metals.

Evans and Lee (*15*) have studied the electrolysis of ether solutions of Grignard reagents, in which magnesium is deposited quantitatively at the cathode while hydrocarbons are liberated at an inert anode. As an example of anodic oxidation may be mentioned the preparation of anhydrous zinc, ferric, copper, and aluminum acetates by the electrolysis of alkali acetates in acetic acid, the respective metals serving as anodes (*16*).

Although a great variety of voltaic cells with non-aqueous electrolytes has been constructed and studied, experimental difficulties have usually prevented the attainment of a high degree of reproducibility in their preparation. Electrometric titrations made by means of such cells have already been mentioned. As recent instances of highly accurate determinations of the electromotive force of non-aqueous cells may be cited the work of Tarbutton and Vosburgh (*17*) on lead-mercurous acetate cells with acetic acid as solvent, and that of Yost and co-workers (*18*, *19*) on cells in liquid ammonia solution. The latter studied the cells Zn (amalgam), $ZnCl_2 \cdot 6NH_3$(s), NH_4Cl (in NH_3,l), TlCl(s), Tl(amalgam) and Zn(amalgam), $ZnCl_2 \cdot 6NH_3$(s), NH_4Cl (in NH_3,l), $CdCl_2 \cdot 6NH_3$(s), Cd (amalgam), and calculated the changes in standard free energy and in heat content for the cell reactions, from the measured electromotive forces and their temperature coefficients. The electrodes used are stated to be suitable for use as reference electrodes in liquid ammonia solution, and provisional values are given for their standard potentials with reference to the standard hydrogen electrode in liquid ammonia.

In the author's laboratory an analog of the familiar lead accumulator, with lead tetra-acetate serving as oxidizing agent and a normal solution of sulfuric acid in anhydrous acetic acid as electrolyte, has been found to give an electromotive force of 1.98 volts.

SALT EFFECTS ON SOLUBILITIES

The familiar effect of salts in increasing the solubility product of other salts is, of course, not peculiar to aqueous solutions. In fact, since activity coefficients of electrolytes decrease more rapidly with increasing concentration in media of low dielectric constant than in water, this salt effect is usually considerably greater in non-aqueous solutions. Solubility studies have recently been made by Seward (*20*) on solutions in ethylene, and by Seward and Hamblet (*21*), Scholl, Hutchison and Chandlee (*22*), and Geer (*23*), on solutions in acetic acid.

The relative magnitudes of salt effects in water and in acetic acid are compared in Figure 1. Here the

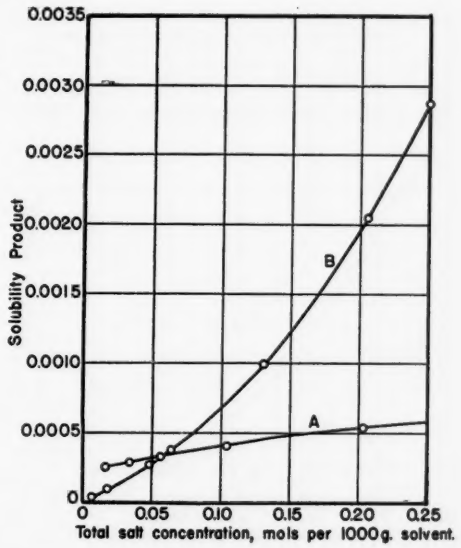

FIGURE 1.—SALT EFFECTS ON SOLUBILITY PRODUCT IN WATER AND IN ACETIC ACID
A—TlCl in aqueous KCl solution at 25°
B—$AgNO_3$ in acetic acid solution of $LiNO_3$ at 30°

variation of the solubility product of silver nitrate in acetic acid solutions of lithium nitrate (*23*) has been plotted, together with the classic data for thallous chloride in aqueous solutions of potassium chloride (*24*). In Figure 2 the actual solubilities of these same salts are plotted, and it is interesting to note that in the acetic acid solutions the effect of the common ion in depressing the solubility of the silver nitrate is soon outweighed by the salt effect; so that after passing through a minimum the actual solubility, as well as the solubility product, increases rapidly with increasing concentration of added salt.

ACIDITY AND BASICITY

According to the widely accepted ideas of Brønsted (*25*), an acid, A, and its corresponding base, B, are related by the equation

$$A \rightleftharpoons B + H^+ \qquad (1)$$

and the acid strength is best defined by the acidity constant

$$K_{acid} = a_H + \frac{c_B}{c_A}$$

where a_{H^+} is the proton activity and c_B and c_A are the concentrations of the base and acid, respectively. Since free protons do not exist in solution to any appreciable extent, equation (1) does not represent an observable process, but we always actually have to consider the protolytic reaction

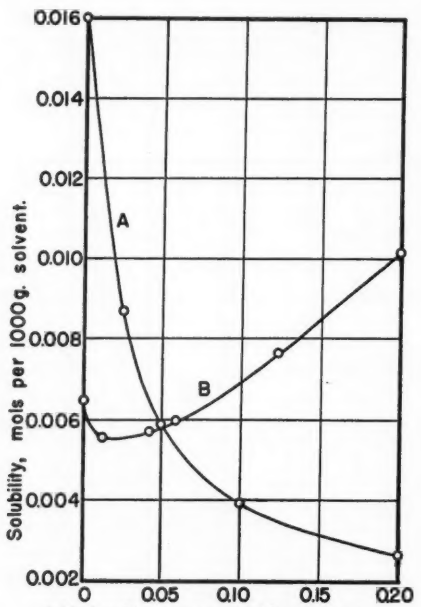

FIGURE 2.—COMBINED COMMON ION AND SALT EFFECTS ON SOLUBILITY
A—TlCl in aqueous KCl solution at 25°
B—$AgNO_3$ in acetic acid solutions of $LiNO_3$ at 30°

$$A_1 + B_2 \rightleftharpoons A_2 + B_1 \qquad (2)$$

where A_1, B_1 and A_2, B_2 are two corresponding acid-base pairs, one of which may be provided by the solvent. The equilibrium constant of this reaction, defined by

$$K = \frac{c_{A_2}c_{B_1}}{c_{A_1}c_{B_2}} \qquad (3)$$

evidently gives the ratio of the acidity constants of the two acids involved and, if one acid-base pair is kept the same, the acid strengths of a series of other pairs may be compared by means of this constant.

It is evident from equation (2) that the extent of dissociation of an acid or of a base will increase with increasing basicity or acidity, respectively, of the solvent. Hence the use of non-aqueous solutions for acid-base studies greatly extends the range of acidities that can be investigated. In the strongly basic solvent ammonia, phenols and acid amides are strong acids, while in the very acid solvent hydrogen fluoride, as has been mentioned above, even nitric acid behaves as a base. The utility of strongly acid media for the study of bases which are too weak to measure in water has been demonstrated by Hall and co-workers (*26*) for glacial acetic acid and by Hammett and co-workers (*27*) for anhydrous formic acid and for sulfuric acid-water mixtures. Again, by the use of an indifferent or aprotic solvent such as benzene, it is possible to avoid the leveling effect by virtue of which, in aqueous solution, all acids appreciably stronger than oxonium ion, OH_3^+, and all bases stronger than hydroxyl ion, are practically completely dissociated and appear equally strong (*28*).

The concentration measurements necessary for the evaluation of the equilibrium constant defined by equation (3) are most readily made in the case of indicators, where the acid and corresponding base are of different colors and colorimetric methods can be employed. Recently Flexser, Hammett, and Dingwall (*29*) have shown that similar methods can be extended to the case of colorless substances by the use of ultraviolet spectrophotometry.

Since equation (3) is equivalent to

$$K = \frac{a_{A_2}a_{B_1}}{a_{A_1}a_{B_2}} \cdot \frac{f_{B_2}/f_{A_2}}{f_{B_1}/f_{A_1}}$$

where a is the activity and f the activity coefficient of the substance in question, it is evident that the value of K will be independent of the medium, and hence a universally valid measure of relative acidities, only in so far as the quotient f_B/f_A remains constant for various acid-base pairs in a given medium. This condition appears to be approximately, though by no means exactly, true for acids of the same charge type. The order of acid strengths has been shown by M. and M. L. Kilpatrick (*30*) to be roughly the same, for acids of the same type, in the basic solvent acetonitrile as in water, and a similar relationship has been found by Brønsted and co-workers (*31*) to hold for the acid solvent *m*-cresol.

Hammett and Deyrup (*32*) propose to measure the acidity of any solution by means of an acidity function, H_0, defined by the equation

$$H_0 = \log \frac{c_B}{c_{BH^+}} + pK'_B$$

where B is an uncharged base and BH^+ the corresponding acid, and pK'_B is the negative logarithm of the thermodynamic dissociation constant of the acid. It is evident that the above definition is equivalent to

$$H_0 = -\log a_{H^+} \frac{f_B}{f_{BH^+}}$$

and that this acidity function becomes equal to the familiar pH in dilute aqueous solution. The value of H_0 at a given acidity is independent of the indicator used to measure it as long as the ratio f_B/f_{BH^+} for various indicators in the same medium remains the same. This condition has been found to be approximately satisfied over a wide range of acidities in mixtures of sulfuric, nitric, hydrochloric, and perchloric acids with water, as well as in anhydrous formic acid (*33*). Hammett and Paul (*34*) have shown that the velocity constants of several acid-catalyzed reactions can be correlated with the acidity function of the medium.

Wynne-Jones (*35*) has discussed the variations of relative acid strengths in media of varying dielectric constant from the point of view of electrostatic theory, and has derived an equation which agrees with the data for water and the lower alcohols. It is certain, however, that especially in media of low dielectric constant, specific chemical factors, and not merely electrical forces, enter into the determination of the activity coefficients and therefore influence relative acidities.

VARIATION OF CONDUCTANCE AND OF OSMOTIC PROPERTIES OF ELECTROLYTES WITH CONCENTRATION

Up to this point, since we have been dealing with general properties of electrolytes, we have emphasized the resemblances, rather than the contrasts, between aqueous solutions and those in other media; but when we turn to the consideration of the variation of thermodynamic properties or of conductivities of solutions with concentration, wide individual differences, due to the special characteristics of the solvent, force themselves upon our attention. During the unquestioned supremacy of the Arrhenius theory, the failure of nonaqueous solutions to conform to the simple relationships which were observed for water solutions led the former to be regarded as exceptional or anomalous. Thus, for example, the values of the so-called degree of dissociation, α, as calculated from conductivity data by the equation

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

(where Λ is the equivalent conductance and Λ_0 the limiting equivalent conductance at infinite dilution), and from freezing-point data (or from any other of the colligative properties of dilute solutions) by means of

$$\alpha = \frac{i - 1}{\nu - 1}$$

(where i is the van't Hoff factor and ν the number of ions produced by the dissociation of one molecule), agreed fairly well in water, at least for dilute solutions of uni-univalent salts, but showed the widest divergence in other solvents, especially in those of low dielectric constant (*36*, *37*). With the general acceptance of theories of complete ionization of strong electrolytes in aqueous solution, it became evident that neither of the above methods for calculating the degree of dissociation was valid, and any agreement between them was therefore merely fortuitous, while a more probable explanation for the decrease in activity coefficient and in equivalent conductance with increasing concentration was to be sought in the effects of interionic forces. Hence, when the limiting laws derived, on the assumption of complete dissociation, from the Debye-Hückel (*38*) and Onsager (*39*) theories * of the ion atmosphere were found to account so satisfactorily for the properties of dilute aqueous solutions of electrolytes, it was hoped that the application of the same theories to nonaqueous solutions would make it possible to interpret their "anomalous" behavior also.

These expectations were, indeed, realized, in the case of very dilute solutions of uni-univalent electrolytes in a few solvents of not too low dielectric constant. Thus, for example, Schreiner and Frivold (*40*) determined the freezing-point depressions of several uni-univalent salts in cyclohexanol (dielectric constant = 15) at concentrations down to 0.0004 molar, and found that the curve of $1 - \varphi$ against $\sqrt{c}$ approached the theoretical straight line of the Debye-Hückel limiting law. A better test of the theory is supplied by solu-

* These limiting laws may be expressed in the following forms. For the osmotic coefficient, φ, defined by the equation $\varphi = \frac{\theta}{\nu\lambda c}$, where θ is the observed freezing-point depression at concentration c and λ the molar freezing-point lowering at infinite dilution, the Debye-Hückel limiting law is

$$1 - \varphi = \beta\sqrt{c}$$

where β is a constant whose value depends upon the temperature, the dielectric constant of the solvent, and the valence type of the salt. (It may be noted here that $1 - \varphi$ is the same, in dilute solution, as the Lewis and Randall divergence function, j). For the activity coefficient, f (defined as the ratio of activity to concentration), the limiting law may be written

$$\log_{10} f = -A\sqrt{c}$$

where A is $\frac{3\beta}{2.303}$.

The Onsager equation for the conductivity of a very dilute solution is of the form

$$\Lambda = \Lambda_0 - (a\Lambda_0 + b)\sqrt{c}$$

where a and b are constants whose values depend upon the dielectric constant, the temperature, the valence type of the salt, and in the case of b upon the viscosity of the solvent also.

The concordance between the values of α as obtained from conductance and from freezing-point data for dilute aqueous solutions may now be interpreted in the following way. For a uni-univalent electrolyte, $\frac{i - 1}{\nu - 1} = i - 1 = 1 - 2j$. Hence, according to the Debye-Hückel limiting law, α (from freezing point) $= 1 - 2\beta\sqrt{c}$; while from the Onsager equation α (from conductance ratio) $= 1 - \left(a + \frac{b}{\Lambda_0}\right)\sqrt{c}$. It is evident that these two equations for α are of the same form. Now in the case of aqueous solutions, as it happens, not only are these limiting equations valid to appreciable concentrations, but the values of the constants β, a, and b, and of Λ_0 for typical salts, are such that the coefficients of $\sqrt{c}$ (2β in one case and $a + \frac{b}{\Lambda_0}$ in the other) are often approximately equal. In the case of other solvents, the values of dielectric constant, viscosity, and mobility of the ions are not such as to bring about a similar coincidence.

bility measurements. In this field, the data of Williams (*41*) and of Brønsted and co-workers (*42*) showed that the activity coefficients of uni-univalent salts in very dilute solution in methyl alcohol (dielectric constant = 30) varied with the square root of the ionic strength in accordance with the limiting law, but that this was no longer true for bi-univalent salts. In the case of acetic acid, a solvent of still lower dielectric constant ($D = 6.2$), while the f-$\sqrt{\mu}$ curves (where μ is the ionic strength) obtained from measurements of solubility (*21, 22*) and of electromotive force (*43*) do indeed appear to *approach* the straight line corresponding to the limiting law, reliable data cannot be obtained at sufficiently low concentrations to afford evidence of actual concordance between experiment and the theory in its simplest form. In these cases, it is true, the experimental results have been fairly well accounted for by the application of various modifications of the Debye-Hückel theory, such as the Gronwall, La Mer, and Sandved (*44*) or La Mer, Gronwall, and Greiff (*45*) extended equations, but such calculations can be made only by the assignment of somewhat arbitrary values, considerably larger than those used for aqueous solutions, to the parameter representing the distance of closest approach of the ions (*21, 22, 43, 46*); hence, the agreement attained can scarcely be regarded as other than empirical.

With regard to conductivity data, the situation is similar to that just described. For non-aqueous solutions, the Λ-$\sqrt{c}$ curve has been found to approach the straight line corresponding to the Onsager equation only in the case of uni-univalent salts, at extreme dilutions, in solvents of dielectric constant higher than 30. Thus Coates and Taylor (*47*) found the equation applicable to solutions of salts in liquid hydrogen cyanide ($D = 95$) over a concentration range from 0.0001 to 0.005 molar. But while Unmack, Murray-Rust, and Hartley (*48*) showed that the conductances of uni-univalent salts in methyl alcohol ($D = 30$) agreed very well with the theory, Barak and Hartley (*49*), on the other hand, in similar experiments in ethyl alcohol ($D = 23$) found agreement between calculated and observed slopes of the Λ-$\sqrt{c}$ curves only in a few instances. In most cases the rate at which the conductance fell off with increasing concentration was greater than that predicted by the Onsager equation, suggesting that the hypothesis of complete dissociation of salts in this solvent may have been incorrect.

The extent and the nature of the deviation of the observed osmotic effects, in a solvent of low dielectric constant, from those predicted by the Debye-Hückel equation, are brought out by Figures 3 and 4. In Figure 3, the logarithm of the activity coefficient, γ (defined as the ratio of activity to molality), of sodium acetate in acetic acid as calculated from freezing-point data (*50, 51*), is plotted against the square root of the molality, m; the straight line corresponds to the Debye-Hückel limiting law, which in this case takes the form $\log \gamma = -25\sqrt{m}$. In Figure 4, $\log \gamma$ is plotted against $\log m$, and here it is evident that the data fall upon a straight line whose slope is $-1/2$; in other words, over a considerable concentration range, the activity coefficient is inversely proportional to the square root of the molality. This relationship, which is in accord with the observations of Hall and Werner (*52*) on the change of hydrogen-ion activity with dilution in similar solutions, is obviously quite at variance

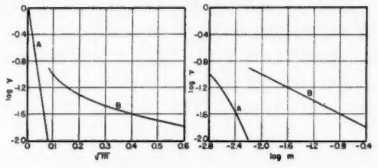

FIGURE 3 FIGURE 4

VARIATION OF ACTIVITY COEFFICIENT WITH CONCENTRATION IN ACETIC ACID AS SOLVENT

A—Debye-Hückel limiting law for 1:1 electrolytes

B—Sodium acetate, from freezing-point data

with the behavior to be expected of a completely dissociated electrolyte subject to the action of forces due to the ion atmosphere. On the other hand, it is just what we should expect of a weak binary electrolyte whose dissociation is determined by the law of mass action, the activity coefficients of the ions remaining constant.*

Similar results have been obtained for several other electrolytes in the same solvent. Thus, for example, Eichelberger (*53*) measured the freezing-point depression for solutions of ammonium nitrate in acetic acid, and found that the divergence function j, at concentrations from 0.005 to 0.05 molal, remained practically constant at a little more than 0.5. This behavior can easily be shown to correspond to an inverse proportionality between the activity coefficient and the square root of the molality.†

Heston and Hall (*54*) studied the activity of hydrogen chloride in acetic acid by means of electromotive force measurements, obtaining results in accord with the vapor pressure data of Rodebush and Ewart (*55*); for this solute, also, the activity coefficient is proportional,

* For such an electrolyte, in dilute solution, we should have the relationship $\frac{\alpha^2 m}{1-\alpha} = K$, where α is the degree of dissociation and K the dissociation constant. If α is small, this may be written in the approximate form $\alpha^2 m = K$, or $\alpha = \sqrt{K} \cdot \frac{1}{\sqrt{m}}$; and, if the ions behaved as perfect solutes, the stoichiometrical activity coefficient would be the same as the degree of dissociation.

† The change in the activity coefficient between two values of the molality is given by the equation $\ln \frac{\gamma_2}{\gamma_1} = -\Delta j - \int_{m_1}^{m_2} j d \ln m$; if j is constant, this becomes $\ln \frac{\gamma_2}{\gamma_1} = -j \ln \frac{m_2}{m_1}$. Hence γ is inversely proportional to m^j, or to $\sqrt{m}$ if j is 0.5. It is obvious that this proportionality cannot continue down to infinite dilution, where j must be zero.

over a wide concentration range, to the inverse square root of the molality. It is evident, then, that the ion atmosphere theory is quite inadequate to account for

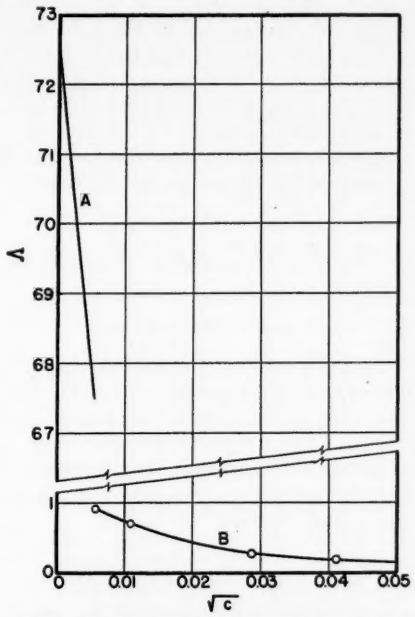

FIGURE 5.—EQUIVALENT CONDUCTANCE OF SODIUM ACETATE IN ACETIC ACID AS SOLVENT
A—Limiting slope according to Onsager equation
B—Data of Kolthoff and Willman

the activity coefficients of electrolytes at experimentally accessible concentrations in this solvent.

The variation of conductance with concentration, for dilute solutions of sodium acetate in acetic acid, is shown in Figures 5 and 6. In Figure 5 the equivalent conductance, Λ, as determined by Kolthoff and Willman (*56*), is plotted against the square root of the concentration. The coefficient of $\sqrt{c}$ in the Onsager equation cannot be determined exactly, since Λ_0 is not known; the straight line in the plot, based on an estimated value of Λ_0, corresponds to the equation $\Lambda = 72.5 - 923\sqrt{c}$. It is evident that the Onsager equation is of no value in predicting the course of the curve at accessible concentrations. In Figure 6, log Λ is plotted against log c; over a considerable concentration range, the curve approximates a straight line whose slope is $-1/2$, indicating that the equivalent conductance is inversely proportional to the square root of the concentration. This relationship, again, is not at all what we should expect of a completely dissociated salt, the mobility of whose ions decreases with increasing concentration because of interionic forces; but it does correspond to the behavior of a slightly dissociated electrolyte.*

* For such an electrolyte, according to the dilution law, we have $\Lambda^2 c = \Lambda_0(\Lambda_0 - \Lambda)K$. If Λ is negligible compared with Λ_0, this becomes $\Lambda^2 c = \Lambda^2_0 K$, or $\Lambda = \Lambda_0\sqrt{K}.\frac{1}{\sqrt{c}}$.

At a concentration just above the range of these data, however, the conductance goes through a minimum; this point will be discussed later.

Similar results were obtained for lithium chloride solutions in acetic acid. Further Hall and Voge (*57*) and Weidner, Hutchison, and Chandlee (*58*) have measured the conductance of sulfuric acid in the same solvent, and have found that it also behaves as a weak electrolyte from a concentration of 0.01 molar to extreme dilutions.

Examples like the foregoing might be multiplied almost indefinitely. It is evident, then, that many typical salts persist in behaving like weak electrolytes in solvents of low dielectric constant, even at the highest attainable dilutions. Perhaps, after all, this conclusion should have been anticipated, for Kraus (*59*) had long since pointed out that the behavior of salts in dilute solution in liquid ammonia closely approximates that predicted by the law of mass action, and had suggested that this law may be approached as a limit, at low concentrations, in non-aqueous solvents in general.

In this connection the extensive and painstaking conductance studies of Walden and his co-workers, extending over a period of many years and including the widest possible variety of solvents, should not go

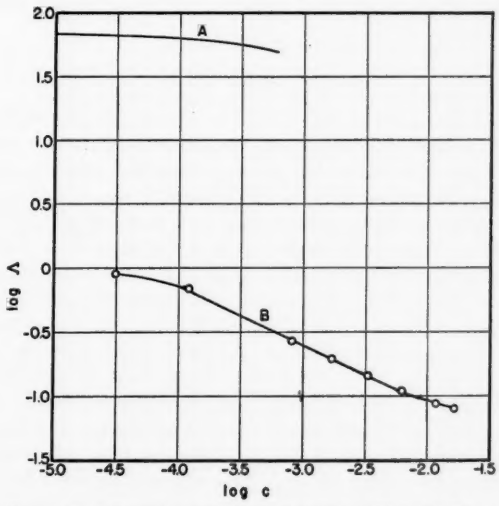

FIGURE 6.—EQUIVALENT CONDUCTANCE OF SODIUM ACETATE IN ACETIC ACID
A—Onsager equation
B—Experimental data

unmentioned. Among solvents recently studied by these investigators are pyridine (*60*), nitromethane, nitrobenzene (*61*), aniline (*62*), acetophenone, cyclohexanone (*63*), and hydrazine (*64*). In the last named medium, an unusual type of ionization is encountered

in the case of aromatic nitro-compounds, which apparently ionize according to the equation

$$RNO_2 + N_2H_4 = RNO_2^+ + N_2H_4^-,$$

an electron being transferred from a solute to a solvent molecule (*65*).

In the papers just mentioned, the departure of the behavior of electrolytes from that predicted by the Onsager theory is repeatedly discussed. While the $\Lambda - \sqrt{c}$ curves are often linear, their slopes are usually much greater than the theoretical value. The tendency of typical salts to behave as weak electrolytes in solvents of low dielectric constant is also emphasized. A distinction is drawn between "leveling" solvents such as water, the lower alcohols, ammonia, and hydrazine, and "differentiating" solvents such as hydrocarbons and their chlorine derivatives, ketones, nitrocompounds, and aniline. In the case of the former group there is considerable tendency toward solvation, which increases dissociation and brings about similarity in the behavior of all salts, while in the latter group a wide variety of individual peculiarities is observed.

The transference number of barium ion in a sulfuric acid solution of barium bisulfate has been measured by Hammett and Lowenheim (*66*) and found to be surprisingly small. The authors suggest that a large part of the conductance of such a solution depends upon proton jumps from sulfuric acid molecules to adjacent bisulfate ions, rather than upon simple ionic migration.

IONIC ASSOCIATION

We now turn to the question of how the incomplete dissociation of true salts in non-aqueous solutions may be reconciled with the now generally accepted idea that, since there can be no chemical bonds between the ions of such compounds, no unionized salt molecules can be present in their solutions. The most promising method of attacking this problem appears to be that first proposed by Bjerrum (*67*, *68*). He suggested that a pair of oppositely charged ions within a certain critical distance of each other may be so firmly bound by electrostatic forces that they do not take part in conduction, nor contribute to the ion atmosphere of other ions. The proportion of such short-range ion pairs to the total number of ions is greater, the lower the dielectric constant of the solvent, the smaller the ions and the greater their charges; it also varies with concentration according to the law of mass action. From this point of view, in order to account for the change of conductance with concentration in a solvent of low dielectric constant, it is necessary to consider not only the change in mobility of the free ions due to long-range ionic forces, but also the change in the relative numbers of free and paired ions, which follows the formal laws of the dissociation theory.

These ideas have been successfully applied to the interpretation of conductance in a brilliant series of articles by Kraus and Fuoss. For a uni-univalent electrolyte in dilute solution in a solvent of not too low dielectric constant (>10) their treatment (*69*) may be summarized as follows. If $1-\alpha$ is the degree of association (or the fraction of the salt which is in the form of ion pairs) at the total concentration c, the concentration of free ions is αc. The sum of the mobilities of the ions, or the equivalent conductance, Λ_c, of the completely dissociated electrolyte at this ion concentration would be, according to the Onsager equation for the effect of the ion atmosphere

$$\Lambda_c = \Lambda_0 - (a\Lambda_0 + b)\sqrt{\alpha c}$$

Hence for the actual equivalent conductance, Λ, or $\alpha\Lambda_c$, we have

$$\Lambda = \alpha[\Lambda_0 - (a\Lambda_0 + b)\sqrt{\alpha c}] \qquad (4)$$

Now, the law of mass action may be applied to the dissociation of ion pairs, provided we employ the activities of the ionic species involved, rather than their concentrations. Using f to denote the mean activity coefficient of the ions (not the stoichiometric activity coefficient), and assuming the ion pairs to behave like neutral molecules, we have

$$\frac{\alpha^2 f^2 c}{1-\alpha} = K \qquad (5)$$

The activity coefficient, according to the Debye-Hückel theory, varies with the concentration of free ions as indicated by the equation

$$\log f = -A\sqrt{\alpha c} \qquad (6)$$

We thus have three equations, (4), (5), and (6), expressing implicitly the relationship between Λ and c, but involving also the variables α and f (which depend upon c) and the constants K and Λ_0.

Before going further, it should be noted that, if K is large, ion association is negligible, α is practically unity, and (4) reduces to the simple Onsager equation

$$\Lambda = \Lambda_0 - (a\Lambda_0 + b)\sqrt{c}$$

If, on the other hand, K is very small, ion atmosphere effects are negligible, $\alpha = \frac{\Lambda}{\Lambda_0}$, $f = 1$, and $1 - \alpha$ may be replaced by unity. Hence from equation (5) we get

$$\Lambda = \Lambda_0\sqrt{K}\cdot\frac{1}{\sqrt{c}}$$

or Λ is inversely proportional to $\sqrt{c}$ under these conditions.

In the general case, because of the varying types of relationship expressed in equations (4), (5), and (6), it would be exceedingly difficult to obtain an explicit solution for Λ as a function of c. Fuoss and Kraus, however, devised an ingenious graphical method of solving the problem, and a simpler method was given by Fuoss in a later article (*70*). The values of K and of Λ_0 for a particular system are found from the conductance data by an extrapolation method; once these are known, the theoretical course of the conductance

curve may be calculated. Fuoss and Kraus carried out such calculations for a wide variety of solvents and electrolytes and obtained very close agreement with experimental data up to ion concentrations of several thousandths molar. Shedlovsky and Uhlig (*71*) applied the same method to their conductance data for sodium and potassium guaiacolates in guaiacol with equal success. The upper limit of concentrations to which this treatment is applicable is set by Fuoss in a recent paper (*72*) at $c = 3.2 \times 10^{-7}D^3$ at 25° for uni-univalent electrolytes. Above this limit, specific ionic interactions of higher order than pairwise become appreciable, and the values of Λ are greater than those calculated by the means just discussed.

Fuoss and Kraus (*73*) next take up the problem of the variation of the dissociation constant with the dielectric constant of the solvent. They consider the distribution, around a given ion, of ions of opposite charge, and regard a pair of unlike ions as being associated when the distance between them is less than a critical value, $\frac{e^2}{2DkT}$, where e is the charge on either ion, D is the dielectric constant, k is Boltzmann's constant, and T the absolute temperature. On the basis of this assumption, an equation is derived expressing K as a function of the dielectric constant, the temperature, and a parameter, a, related to the sizes and configurations of the solvated ions. [An improved method of calculation, leading to very nearly the same result, is given in later papers by Fuoss (*74*, *75*).] The equilibrium constants calculated in this way are found to agree with experimental data over a wide range of dielectric constants. Thus, for tetraisoamylammonium nitrate in dioxane-water mixtures, K is found to vary, as predicted, from 2×10^{-16} in pure dioxane, for which D is 2.4, to 0.25 in a mixture (53 per cent. water) for which D is 38; for values of D greater than 44, the equilibrium constant theoretically becomes infinite, corresponding to complete dissociation.

The authors next turn (*76*) to the course of the conductance curve at concentrations beyond the upper limit to which we have previously referred, and particularly to the problem of the conductance minimum which is always observed in solvents of low dielectric constant (<20). (In benzene and dioxane, these minima occur at concentrations of the order of 0.00001 molar.) They account for this phenomenon by postulating a reaction between ion pairs, or dipoles, and free ions, according to the equations

$$AB + A^+ \rightleftharpoons A_2B^+$$
$$\text{and } AB + B^- \rightleftharpoons AB_2^-$$

With the aid of the not implausible assumption that these two reactions take place to the same extent, and neglecting the long-range interionic effects, which would be very slight in solutions of small total ion concentration, it is shown that the conductance function takes the form

$$\Lambda = Ac^{-1/2} + Bc^{1/2}$$

the first term representing the conductance due to simple ions, the second that due to the triple ions; A and B are constants whose values depend upon the respective limiting conductances and equilibrium constants.

Differentiation of this equation with respect to c shows at once that Λ will have a minimum value at a concentration $c_{min.}$ whose value is given by the equation

$$A = Bc_{min.}$$

Obviously, at this concentration, $Ac_{min.}^{-1/2} = Bc_{min.}^{1/2}$; that is, the minimum occurs when the conductance due to free ions is just equal to that due to ion triples.

With increasing dielectric constant of the solvent it becomes necessary to consider ion atmosphere effects on mobility and activity. As in the case of ion pairs, the dissociation constant, k, of the triple ions is dependent upon the temperature, the dielectric constant, and the ion sizes; and again, the values of k calculated for tetraisoamylammonium nitrate in various dioxane-water mixtures are shown to be in agreement with the experimental data. With increasing dielectric constant, k increases and the point at which the minimum conductance occurs shifts toward higher concentrations. Over a considerable range, it is found that $c_{min.}$ must be proportional to D^3; so that a theoretical basis is supplied for a relationship which was previously discovered by Walden (*77*), who expressed it in the form of the empirical rule, $D^3V_{min.}$ = constant, where $V_{min.}$ is the dilution at which the minimum appears. Above a critical value for the dielectric constant, however, triple ions are no longer stable, and the conductance minimum therefore eventually disappears.

In the case of tetraalkylammonium salts in pure dioxane or in benzene (*78*), the form of the conductance curve beyond the point of minimum conductance becomes rather complex. This fact is attributed to the formation of clusters containing more than three ions; association appears to increase very rapidly with increasing concentration, once the triple ion stage has been passed. This hypothesis is supported by freezing point data for salts in dioxane (*79*) and in benzene (*80*); at concentrations of the order of 0.0001 molar, the apparent molar weights of the solutes approach the formula weights, indicating practically complete association to ion pairs, while at higher concentrations there is evidence of the formation of much larger aggregates. Thus the apparent molar weight of tetraisoamylammonium thiocyanate in 0.02 molar solution in benzene is approximately eleven times the formula weight.

Such ion pairs as have been discussed here might be expected to exhibit rather large dipole moments. Measurements of the dielectric constants of dilute solutions of salts in benzene by Hooper and Kraus (*82*) have shown these compounds to have very high molecular polarizations, which usually decrease with increasing concentration due to the formation of more complex structures.

The interpretation of the behavior of electrolytic solutions in terms of ion association must inevitably raise the question of whether the new viewpoint does not represent a return to the classical Arrhenius theory. Walden, for instance, brought up this point six years ago when he inquired (of Bjerrum, presumably) (*77*), "Are not these 'enormously firmly bound ion pairs' in the solution practically the same as the previously assumed undissociated molecules?" An adequate reply to this question may perhaps be found in a recent statement by Fuoss (*81*), " 'Formation of ion pairs' is a convenient and short way of expressing the fact that, when the potential energy $\frac{e^2}{a\,D}$ of two oppositely charged ions at contact becomes large compared to the thermal energy $k\,T$, we find more and more configurations of ions in which two such ions spend a relatively large fraction of their existence very near to each other. The phrase does not imply the formation of chemically neutral molecules. There are cases where, after Coulomb forces have brought two ions into contact, the electrons in the two ions redistribute themselves in accordance with quantum restrictions, to form a homopolar bond. Then in these cases the formation of the final neutral molecules cannot be described simply by means of Coulomb's law."

The problems presented by non-aqueous solutions of electrolytes have evidently not yet been solved. No adequate theory has as yet been proposed for concentrated solutions. The influence of specific chemical relationships of solute and solvent has repeatedly been emphasized (*83*). Study of the increase in conductance in very strong fields (Wien effect) and at very high frequencies (Debye effect), the consideration of which would be beyond the scope of this article, promises to throw further light upon the influence of the ionic atmosphere (*84*). The conductance of fused salts, of which very little is known, presents another field for future investigation. The work of the past few years, however, has undoubtedly indicated the paths along which further progress is likely to be made toward the understanding of electrolytic solutions.

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A PRECISE *and* RAPID METHOD *of* BRINGING *a* PRECIPITATE *upon a* FILTER*

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THE USUAL method of quantitatively bringing a precipitate onto a filtering medium is quite irrational. To decant the liquid, to guide the precipitate down a stirring rod, to rinse the beaker held in one hand with a jet from a wash bottle held in the other hand, are operations which not only require considerable skill but consume much time. The method described below is much simpler and more sensible. We have found that it is quite feasible to run the precipitate onto the filter directly from the bottom of the vessel in which the precipitate was formed. The precipitation is carried out in a funnel the stem of which is closed with a rubber tube and clamp. After the supernatant liquid has become clear, the clamp is carefully opened so that the precipitate and liquid may flow of their own accord onto the filter below. Actual tests have proved this simple procedure to be both quantitative and quick.

The funnel used in these trials was eight centimeters high and had a capacity of two hundred milliliters but, if the volume of the liquid concerned indicates the greater suitability of a funnel of another size, no diminution in the reliability of the procedure need be feared. The stem of the funnel was one centimeter across and three centimeters long. The rubber tube was five centimeters long and its lower, free end was cut off at a sharp angle. The stock type of screw clamp with hinged outer jaw is quite satisfactory. The funnel is supported by a ring and ring stand, and adjusted so that the end of the rubber tube extends one centimeter into the glass filtering crucible.

The funnel must be scrupulously cleaned and then thoroughly washed with water, or better with alcohol-ether, so that the precipitate will slide readily. After the funnel is ready, the rubber tube is clamped shut, the funnel is placed on the ring, and ten milliliters of boiling distilled water is run in. This acts as a buffer and fills the bottom of the funnel with water. The solution to be analyzed is slowly introduced from a pipet or buret, distributing the sample around the walls of the funnel. Twenty-five milliliters of boiling water is then added. This effectually heats the contents of the funnel in case the precipitation is to be made from a hot solution. The requisite acid is then dropped in, followed by the precipitation reagent. This is added from a pipet or dropper, with the drops distributed here and there over the surface of the liquid. When the precipitation appears to be completed, the entire contents of the funnel are mixed, not with a stirring rod, but with a jet of boiling water from a wash bottle. The funnel is then covered with a watch glass, or a Petri dish. When precipitated in this manner, the halides of silver coagulate rapidly, and barium sulfate settles readily.

The weighed filtering crucible, brought to constant weight at 130°C., is placed beneath the funnel in a holder which is fitted into a tubulated bell jar so that the filtration can be carried out with the aid of suction (see figure). About two milliliters of the precipitation reagent is put into the crucible to insure that no

* Translated by Ralph E. Oesper, University of Cincinnati, Cincinnati, Ohio.

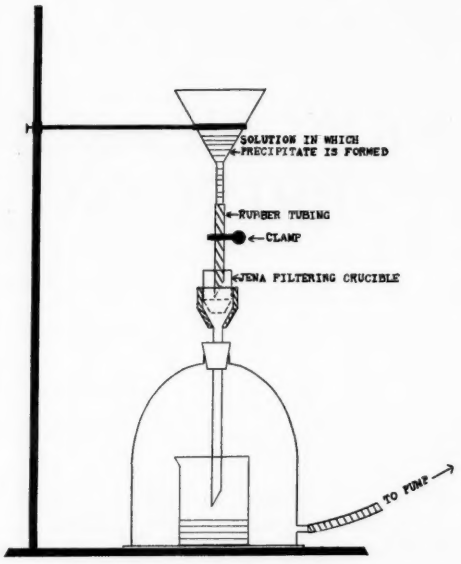
trace of the solution being analyzed escapes reaction. The clamp is opened slightly and the liquid in the funnel, together with a little of the precipitate, begins to drip into the crucible. Most of the precipitate remains in the rubber tube. After a few minutes, the liquid begins to seep through the bottom of the crucible of its own accord, thus thoroughly wetting all the pores of the filter bed. The pump is then cautiously started, lightly at first, and, after a preliminary period of observation, the force of the suction is gradually increased. The filtrate is absolutely limpid. After the liquid has all been removed by this inverse decantation the clamp is opened to its full extent and then taken off the rubber tube. The precipitate is easily washed into the crucible by lightly squirting hot water against the walls of the funnel and into the rubber tube. Three or four such rinsings with small volumes of water suffice to bring the precipitate quantitatively into the crucible. If need be, though the necessity seldom arises, a stirring rod, fitted with a rubber policeman tip, may be used to detach particles still adhering to the funnel or tube, on whose sides they may be easily detected. The washing of the precipitate is completed with water or a suitable wash liquid introduced into the funnel or directly into the crucible itself. The usual tests for completed washing are made on test portions of the filtrate collected in a test tube. The drying of the precipitate and the weighing of the crucible and its contents are carried out in the usual way.

Determinations of known quantities of silver and barium have shown that this procedure gives results that are eminently satisfactory. For silver chloride Jena crucibles No. 1G3 are recommended, for barium sulfate either 1G3 or 1G4.

From the foregoing it is obvious that precipitates can be quantitatively brought onto a filter by this simplified method, but it still remains to be demonstrated that the above conditions will lead to precipitations as complete as those achieved in vessels containing large volumes of liquid, and especially must it be proved that the concentrations and other conditions here available will be as favorable as those prescribed in the methods now in general use. In particular it must be shown that a quantitative precipitation can be effectuated without heating over a flame, without mixing with a glass rod, and without waiting several hours for the liquid to clear and the precipitate to settle completely. If these difficulties do not intervene or can be successfully surmounted, it follows that many gravimetric procedures may be greatly simplified and expedited, because there is no longer a question as to the efficacy of this new, rapid, quantitative transfer of the precipitate onto the filter.

Special studies will have to be made to determine the optimum conditions of precipitation in the various cases that are sure to present themselves. Instances in which large volumes of solution are indispensable can be met by using large funnels. If working at elevated temperatures is absolutely necessary, the working funnel may be inserted into a copper hot-water funnel or the funnel might be heated by means of a steam coil fitted around it.

Likewise, only actual trials can show whether it is better to filter as soon as the precipitate has been produced or whether this operation should be delayed. Our experience has been that prompt filtration is advantageous because this diminishes in a large measure



the entrainment of impurities in the precipitate, a source of much dissatisfaction in current practice.

The discovery of the appropriate concentrations of solutions and reagents to be used in individual cases should offer no particular difficulties. The new procedure is susceptible of considerable modification and probably can be still further simplified by reducing the volume of the solution, and hence the time required to complete the precipitation and filtration. Such developments will depend primarily on further improving the filtering crucibles, either glass or procelain. As soon as these have been brought to the point that perfect filtration of even the finest suspensions is assured, it should be possible to carry out the precipitation, washing, and calcination within the crucible itself, resulting in a speed and possibly a precision beyond anything now known. In fact, preliminary studies have already shown that silver halides, barium sulfate, and copper sulfide can be produced satisfactorily in the crucible itself. If further researches confirm our hopes in this direction, there will remain no other avenues of reducing the time required for these determinations except the time spent at the balance, and the recent developments in weighing devices and balance accessories have already taken us far toward this desirable goal.

THE 1935–36 COLLEGE CHEMISTRY TESTING PROGRAM

Report of the Committee on Examinations and Tests

THE development of the Coöperative Chemistry Tests[1] is a part of a coöperative endeavor of the committee on Examinations and Tests of the Division of Chemical Education and the American Council on Education through its Coöperative Test Service. As educational problems of wide significance arise, the organization obtains grants from foundations for the study of these critical problems. On July 1, 1930, the General Education Board, one of the Rockefeller Foundations, granted a sum of money to the American Council on Education to form a non-profit agency to stimulate the construction, distribution, and use of better tests at the high-school and college level. Dr. Ben D. Wood of Columbia University was chosen to direct the work, and to Dr. R. W. Tyler of Ohio State University was assigned the task of compiling tests in chemistry and some of the other sciences. They are assisted by interested and competent teachers in the subject-matter fields in formulating objectives and in the preparation of and judging material for examinations.

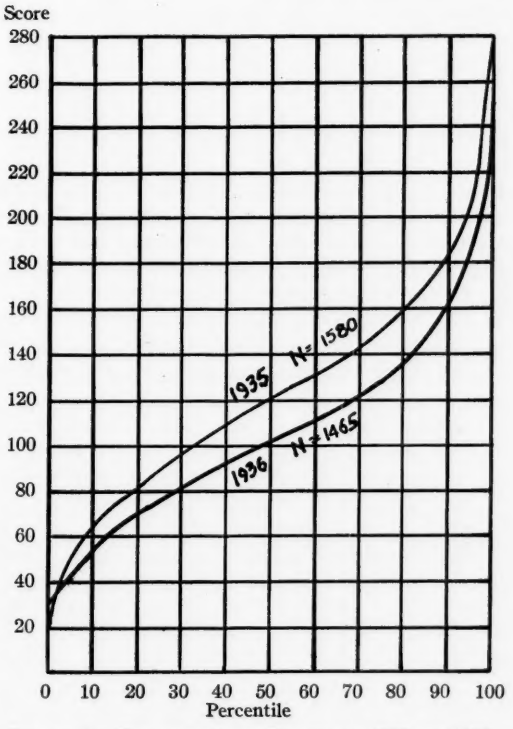


FIGURE 1.—DISTRIBUTION OF SCORES FOR 1935 AND 1936

The physicists[2] have been actively working together in the program for the past three years. They have demonstrated that there is "a fair amount of agreement on core materials for elementary courses and that extent of learning measured relatively can be of practical value to teachers." These values, they state, may be the early identification of the gifted and the "non-physics-minded" students, a means of rating a student on a national as well as local scale, the allocation of transfer students and for evaluating teaching assistants.

This report deals with the results obtained this past year with the 1936 Coöperative Chemistry Tests. Examinations were given with different forms in 1934 and 1935.[3] The 1936 test covers these areas.

Test I	Sections I and II	Selection of Facts and Terminology
	Section III	Formulas, Equations, Problems
Test II	Section I	Interpretation of Experimental Data
	Section II	Application of Principles
Test C	Section I	Selection of Facts
	Section II	Terminology
	Section III	Application of Principles

The number of tests distributed during the past two years is:

	1934–35	1935–36
Chemistry Test I	1597	3068
Chemistry Test II	1339	2118
Chemistry Test C	5209	7194

It is regrettable that only twenty-four liberal arts colleges, nine junior colleges, and just two universities sent in reports on 1465 students. This is about twenty per cent. of the total tests distributed. (See Table 3.) The distribution of institutions is so inequitable, the size of the classes so small, and the number of cases so few that only implications can be shown. The identity of the institutions is not known by the members of the committee; hence, all implications should be impartial.

The distribution of the scores and the number of students in the various classes are shown in Table 1 and the national percentile in Table 2. The scores are not piled up at either end of the scale, hence there is sufficient spread to differentiate the students and the participating schools from one another. Thus, the percentile rank may be readily found by a class or a student. In this manner a student may get

[1] Tests may be obtained from the Coöperative Test Service, 437 West 59th St., New York City.

[2] "The 1935–36 College Physics Testing Program," *The American Physics Teacher*, **4**, 156 (1936).

[3] "The 1935 College Sophomore Testing Program," *The Educational Record*, **16**, 444–81 (1935).

a better understanding of his achievement and may compare his ability with all participating students.

Each score in each column (Table 2) shows the upper limit of the percentile indicated at the extreme right and left of the table. For example, in the total score of Test C all scores of 30 or below have a percentile value of 1; all scores of 31 to 36 a percentile value of 1+ to 3; and the maximum score of the lower 50 per cent. of the 1465 students is 98.

Comparison of the Distribution of Scores.— Good examinations should have the same level of difficulty from year to year. Individuals or small groups of teachers find it hard to devise comparable tests. The distribution of the scores made in Test C in 1935 and 1936 show a close approximation as illustrated in Figure 1. In the case of Tests I and II, using the meager results available, the curves in general follow those given for Test C.

Variability of Achievement.—There are striking differences between colleges and between student abilities in the same and in different institutions. This variance is graphically shown in Figure 2 which shows the percentile distribution of fourteen selected institutions, including that with the lowest and that with the highest median scores. A similar spread is found in other college subjects such as physics, English, etc.

This rather strikingly shows that the poorer students in some schools, as No. 23 or 31, are equally as well prepared as the upper sixteen per cent. of the students in school No. 10 or 38. Even the poorer student in No. 23 or 35 is better than the average student in the upper half of the students of schools 10 and 38. In some

TABLE 1

DISTRIBUTION OF SCORES

Score	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	*Total*	*Score*
240																															1									1	240
30																																								0	
20	1							1																1	1	1	1			1										7	
10																	2						2	1			1				1								1	8	
200					1	1			1		1									2			1	2			1			1				1					1	13	200
90													1	2						1			1	1			4			3			3		1			1	18	
80													1		2	1	1			2		1	1	3									1	2	1				16	
70	1				1				2	1					3	1				2	1		2		2	2	2	1		3		1		2	1	2		2	32	
60		2			1			2	3		1		3	3		1	1		1		3		6	4	2	3	2		2	2	1			4		1		1	49	
150	1					1	1		2	1	1		2	2		1	1	3			1		9	1	1	2		1	1	2	1		4	2				1	43	150
40		1		2					2	3	2		3	2	3	1	3	1	2	3	2		1	3		2	4	1	2		8	1	5	3	4	2	6		2	74	
30	2	2	3		2	1	2		4	1	1	2	4	4	4	1	2	2	1	4	1	1	4	8	1	3	1		6	2	3		3	4	2	7	6	1	2	97	
20	2	5	1		3	2		1	3	5	2		3	7	3	1		3	2	2	3	1	1	1		2	2	2	3		3	3	7	5	4	3	14	1	3	103	
110		1	3	2	1	2	2	1	2	9			7	8	2	1	1	4	1	1	5	3	3	1	1	2	3	3	6	5	3	3	4	2	4	3	14	1		114	
100		1	5		3	2	2	1	5	8	1	1	4	4	4	2	6	2	1	4	13	1	5		2	8	2	1	6	4	2	1	5	4	5	4	15	1	1	136	100
90		3	5		8	1	6	1	6	11	2	1	6	9	5	1		3	3	1	2	2	2	1	1	5	1	1	6	11	5	7	12		7	5	26	3		169	
80		4	2		3		1	3	5	20		1	3	6	9	3	1	3	5	6	5	2	3	1	1	5	3		3	5	5	4	9	1	3		26	2		153	
70	1	5	4		5	1	1	2	1	19	1		8	6	6	2	2	4		1	7	2	2	2	1	5	1	1	1	8	1	3	8	1	1	2	19	2		136	
60		7	4		2	6	2	1	1	20	1		4		6		1	2	4	1	8	4			2	2		1	2	3	1	2	8	1		1	15	1		113	
50		1	3	1		3	1	1		16	1		2	1	2		1	1	1		4				1	4	1		1	1		2	5	1			11	1		67	50
40		5	1	1		1			1	13			2	2	1						5	2			1		1			1		1					12	3		53	
30		4	2			1			2	16			3		3						3	2											1					9	4		48	
20		1															1				2		1		1													1	1	1	8	
10				1									1																									3		5	
No.	8	42	33	7	30	22	18	14	40	143	14	5	57	56	53	18	21	28	21	30	65	21	44	30	18	46	30	11	39	41	44	30	68	27	44	29	179	24	16		0
School	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39		

TABLE 2

NATIONAL PERCENTILES FOR ALL STUDENTS

	Chemistry Test I			*Chemistry Test II*			*Chemistry Test C*				
	Sects. 1 & 2	*Sect. 3*	*Total Score*	*Sect. 1*	*Sect. 2*	*Total Score*	*Sect. 1*	*Sect. 2*	*Sect. 3*	*Total Score*	
No. of Colleges	13	13	13	7	7	7	39	39	39	39	
No. of Cases	454	454	454	384	384	384	1465	1465	1465	1465	
Mean	141.7	69.1	210.5	84.7	23.7	108.5	58.5	26.6	18.1	103.3	
Sigma	45.7	27.9	66.5	21.6	11.4	28.4	21.5	12.4	11.1	40.0	
Percentiles											*Percentiles*
100	283	140	412	130	60	188	130	62	62	245	100
98	237	124	354	118	49	158	108	53	45	199	98
93	215	113	316	110	43	149	94	46	36	168	93
90	207	109	302	109	40	145	88	44	33	159	90
84	189	102	278	106	35	138	80	40	29	143	84
80	180	96	270	105	33	135	76	38	27	136	80
75	172	90	255	103	31	131	72	35	25	129	75
70	165	83	241	101	29	127	68	33	23	122	70
60	149	74	226	95	26	119	62	29	20	109	60
50	138	67	206	90	23	111	57	26	17	98	50
40	126	60	189	81	20	102	52	23	14	90	40
30	116	52	169	73	17	92	46	20	11	80	30
25	110	48	160	68	15	87	44	18	10	75	25
20	100	44	151	64	14	82	40	16	8	69	20
16	95	40	144	61	12	78	37	14	7	64	16
10	85	34	127	53	10	71	32	11	4	55	10
7	79	30	117	48	7	64	28	9	2	48	7
3	59	22	94	41	5	55	22	5	1	36	3
1	52	11	82	32	1	47	15	1	0	30	1

classes there is a small divergence between the better and poorer students, as in No. 33, while in others, as 13 and 31, there is a wide range in ability. (This is illustrated by the short and the long bars.) Too much emphasis should not be placed upon the performance of any one class, as classes vary widely, but if a school occupies a high or low position over a period of years some conclusions may be drawn as to the good or poor qualities of students or teachers. Likewise, the objectives of schools are not the same. The aim and emphasis of the teachers of general chemistry in a liberal arts college may be quite different from that of the technological institutions, or the universities with a consequent and logical variance in the ability of students to score in a given test. Hence, no final conclusions should be drawn unless the aims of the teachers are known.

In comparing the performance of students in the liberal arts colleges, junior colleges, and universities, those from the universities made a much higher score than those from the other two and between these there is no significant difference.

TABLE 3

School	*No.*	*Students*	*Median*
Liberal Arts College	23	905	95
Junior Colleges	9	193	97
Universities	2	74	110

Conclusions.— Since this is the first report by the committee we feel that a word of caution should be given. First, a high score on the tests does not indicate that a department is doing its best for the student because the college, in the light of its aims, may be giving students other experiences far more valuable to them, in view of the students' abilities, interests, and social needs, than a mere mastery of general chemistry.[4] Second, too few cases and an inequitable distribution of schools justify interpretation only as to implications and trends. Certainly, generalizations and conclusions are unwarranted. Third, sufficient data are presented to determine the relative position of a student or a college in comparison to a large number of students and institutions and to show the wide range that exists in the abilities of students and classes.

We wish to thank each department and teacher collaborating in this program. This program depends upon the splendid and cheerful assistance of those teachers who made the necessary experimental studies and those who criticised and made suggestions on the tests. We also wish to give credit to those teachers who have coöperated by using the tests, though questioning and doubting the program. We appreciate their frankness in expressing their opinions and doubts and their generous assistance. It is through this splendid spirit of coöperation that the 1937 chemistry testing program will progress.

[4] "The 1934–1935 College Physics Testing Program," *The American Physics Teacher*, 3, 145 (1935).

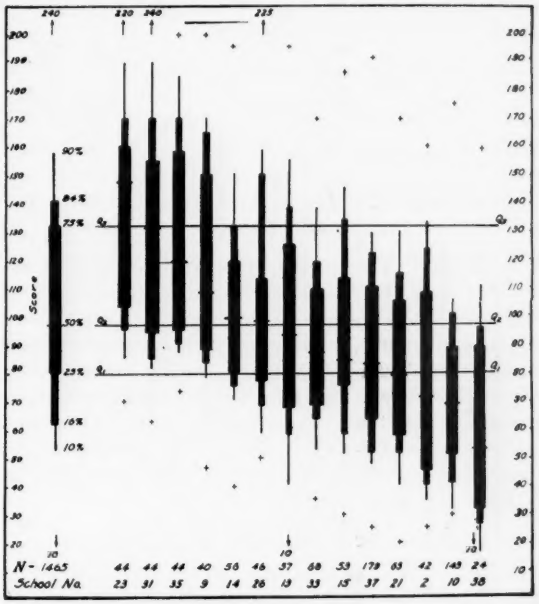


FIGURE 2.—VARIABILITY OF ACHIEVEMENT IN SOME PARTICIPATING COLLEGES. The middle horizontal line shows the national median and the other two lines are at the 25th and 75th percentiles of the national distribution. Each of the bars represents an individual college. The wide portion of each bar represents the range of scores of the middle half in each college. The narrow parts extend to the 16th and 84th percentiles in each college, *i. e.*, one standard deviation above and one below the mean. The lines at the ends extend down to the 10th percentile and up to the 90th percentile. The crosses below the bars represent the lowest scores and those above, the highest scores in the several colleges (the range). The short cross-line at the middle of each bar represents the median score of the college. The bar at the left represents the distribution of all students.

The Committee on Examinations and Tests Division of Chemical Education

B. CLIFFORD HENDRICKS — R. E. KIRK
EARL W. PHELAN — S. R. POWERS
RUFUS D. REED — FRANK B. WADE
O. M. SMITH, *Chairman*

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Secretary-Treasurer, S. A. Chester, Bloomington High School.

Seventy-five were in attendance at the 1937 spring meeting at Normal. New officers for ensuing year: President and Secretary-Treasurer, same as above.

Reported by Howard W. Adams, Illinois State Normal University.

PERIODIC SYSTEM *of the* ELEMENTS *in a* NEW FORM

EMIL W. ZMACZYNSKI

White-Russian University, Minsk, U. S. S. R.

MENDELÉEFF'S PERIODIC LAW AND ITS TABULAR EXPRESSION

PERIODIC recurrence of properties of the elements, discovered by Mendeléeff, is one of the most important laws of nature. This regularity is an objective, absolute truth, but its graphic representation in any tabular form has a subjective character, and up to the present time no one has succeeded in compiling the table in such a way that it could be considered a complete index of all regularities so far as the connection between the properties of elements and their atomic numbers is concerned.

THE DEFECTS OF MENDELÉEFF'S TABLE

If we turn to the table devised by Mendeléeff himself, we shall note some essential defects in it:

(1) qualitatively dissimilar elements, such as manganese and chlorine, chromium and sulfur, and so forth, are placed in one and the same group;

(2) in the table, it is impossible to separate metals from metalloids (non-metals); *i. e.*, electropositive elements from electronegative;

(3) elements which give colorless and diamagnetic ions are not distinguished from those which give colored and paramagnetic ions;

(4) there is no place in the table for the rare-earth metals;

(5) Mendeléeff's table does not reflect the structure of electronic shells of atoms.

THE ABUNDANCE OF PERIODIC TABLES

The abundance of other tables devised during Mendeléeff's lifetime and afterward indicates that the problem of construction of a table which would satisfactorily express the change of the properties of elements in dependence upon their places in the periodic system is not yet solved.[1]

A NEW ESSAY IN THE CONSTRUCTION OF A RATIONAL TABLE

Without pretending to offer an exhaustive solution of the problem, I have, nevertheless, made an attempt to put the P. S. E.* into such a form that it would be possible to eliminate the cited defects in Mendeléeff's table.

THE ENTITY OF THE PERIODIC LAW

First of all, it is necessary to establish the entity of the periodic law and to ascertain what is the periodicity of the properties of elements. That is nothing but reiteration of the preceding phases of evolution of elements—that is, a spiral development.

SPIRAL OR HELICAL FORM OF P. S. E.

It follows from this that the spiral or helical form must be added to the periodic system, as was first done by Chancourtois[2], and afterward by Stoney,[3] Crookes,[4] Harkins and Hall,[5] Antropoff,[6] Clark,[7] and others.

W. Kurbatoff, in his monograph dedicated to Mendeléeff's periodic law,[8] also prefers the helical form of representation to other forms, referring to the fact that the helical form is also characteristic of the development of other systems, such as celestial worlds (nebulae) and rather simple animals (mollusks).

F. Ephraim, in his textbook of inorganic chemistry, also states that it would be more logical to place the elements on the spiral with hydrogen in the middle and other elements arranged in the same vertical groups on the radii.

LAYING THE SPIRAL ON A CONE

Having chosen the spiral form for the P. S. E., I imposed the spiral on a cone, not on a cylinder, as had been done by some previous authors. I did this in such a way that the elements which have the same peripheral structure would be placed one under another, forming the knots of the spiral, along the generatrix of the cone (see Figure 1).

THE TURN OF THE SPIRAL IS EQUAL TO THE WHOLE PERIOD

Every turn of the spiral embraces a complete period.

[1] A complete bibliography and descriptions of several types of graphic classification of the elements are given by G. N. QUAM AND M. B. QUAM, "Types of graphic classifications of the elements," J. CHEM. EDUC., 11, 27, 217, 288 (Jan., Apr., May, 1934).

* P. S. E. is an abbreviation of the words, "Periodic System of Elements."

[2] A. E. B. DE CHANCOURTOIS, "Vis tellurique, classement naturel des corps simples ou radicaux obtenu au moyen d'un systeme de classification helicoidal et numérique," Gauthier-Villars, Paris, **1863**.

[3] G. STONEY, *Chem. News*, **57**, 163 (1888); *Proc. Roy. Soc.*, **85**, 471 (1911).

[4] W. CROOKES, *Proc. Roy. Soc.*, **63**, 498 (1898); *Chem. News*, **78**, 25 (1898); *Z. anorg. allgem. Chem.*, **18**, 72 (1898).

[5] W. D. HARKINS AND R. E. HALL, *J. Am. Chem. Soc.*, **38**, 169 (1916).

[6] A. VON ANTROPOFF, *Z. angew. Chem.*, **39**, 722 (1926).

[7] J. D. CLARK, J. CHEM. EDUC., **19**, 675 (1933).

[8] W. KURBATOFF, "Law of Mendeléeff," Leningrad, **1925**, p. 398 (Russ.).

I consider this to be correct, for each "wave" of Lothar Meyer's curve, which shows the change of so important an elemental magnitude as atomic volume, also em-

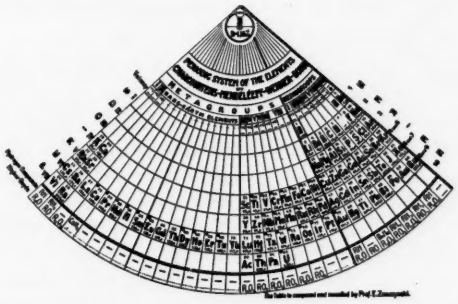


FIGURE 1.—THE TABLE AS COMPOSED AND MOUNTED BY THE AUTHOR

braces the whole period, disregarding the so-called semi-periods.[9]

THE REFLECTION OF DOUBLE PERIODICITY

The double periodicity of the maximum valences with respect to oxygen in long periods is marked in my system with one cone generatrix, which divides long periods into two semi-periods (series); on the table it is drawn as the double line.

THE DIVISION OF THE TABLE INTO SECTORS

In consideration of the important rôles of the numbers 4, 8, and 32 in modern atomic theory, I found it expedient to divide the surface of the cone into thirty-two small sectors, joining them in groups of eight in four large sectors.

THE INCLUSION OF THE RARE-EARTH METALS IN THE SYSTEM

Consequently, the rare-earth metals also found room in my system, although these metals generally have been excluded from similar systems, and considered "Rumpelkammer der Natur," according to the witty remark of one chemist. Their intermediate position between Groups II and III reflects their characteristic peculiarity as expressed in the fact that though they have only two valence electrons, they behave as trivalent elements.

The hiatuses in the long periods, which occur because of the inclusion of the rare earths, may, as will be shown, be interpreted from the point of view of the structure of the atom, whereupon these disruptions will acquire a definite sense (see page 234).

THE CUTTING OF THE CONE'S SURFACE FOR PLANE REPRESENTATION

For the plane reproduction of the system, the most convenient for survey, it was necessary to cut the surface of the cone along one of the generatrices. Periodicity certainly will not suffer from the selection of either line of division (compare Perrin's table, where noble gases are placed in the middle of the table); but it seemed to me that nature itself shows that the line of division must pass in such a way as to indicate the "ends" of the periods, *i. e.*, the places where the structures of the outer electrode shells reach the greatest stability. These "ends" are marked by the noble gases.

A. Haas, in his book "Atomtheorie," also points out that "Die Edelgase stellen so gewissermassen die Marksteine in der natürlichen Reihe der Grundstoffe dar. Durch sie zerfällt die Reihe in sieben Perioden."[10]

THE MARKING RÔLES OF NOBLE GASES AND ALKALINE METALS

After each noble gas a new period begins with an alkaline metal, and alkaline metals, as is well known, occupy "outstanding" positions in the periodic system, disposing themselves on the crests of the waves of Lothar Meyer's curve—that is, on maxima of the curve of atomic volumes.

Exactly the same marking rôle of alkaline metals and noble gases is seen from their position on the curve of ionization potentials,* where the former occupy the minima and the latter the maxima. Hence, it is clear that the surface of the cone must be divided along the line which passes between noble gases and alkaline metals.

THE DIVISION OF GROUPS INTO ORTHO AND META GROUPS

Arranging the elements over the spiral in such a way that they would be located as far as possible toward the right side of the table, *i. e.*, toward the noble gases, we find that the fourth great sector contains, without exception, those elements that have normal structures of electronic shells.†

That is why I named the groups of the fourth sector *ortho groups*, giving them the ordinal numbers corresponding to the numbers of electrons in the outermost shell of the elements in a given group. Thus the group of noble gases must be considered as being the eighth ortho group.

The remaining three large sections of the table, occupied by the groups of elements which have abnormal

[9] P. KIRCHBERGER, "Die Entwicklung der Atomtheorie," Karlsruhe, 1922, p. 62.

[10] A. HAAS, "Atomtheorie," Walter de Gruyter & Co., Berlin and Leipzig, 1924, p. 81.

* "Ionization potential" is the tension, expressed in volts, which is necessary for the separation of one electron from an atom, in consequence of which it becomes an ion with one elementary charge.

† The structure of electronic shells of elements may be described as "normal" when a newly added electron (by increasing the atomic number) places itself on the orbit, the first quantum number of which corresponds to the number of the period in which the given element occurs. Such elements, as is well known, are not indicated in the table of N. Bohr.

Abnormal and twice-abnormal structure of electronic shells consists in the fact that a newly added electron places itself on the orbit, the first quantum number of which is one, or even two, units less than the number of the period in which the given element occurs. In N. Bohr's table such elements are marked by placing them in one, or two, frames, respectively. (See N. Bohr, "Uber den Bau der Atome," Springer, Berlin, 1924, p. 9.)

structures of the electronic shells (except the groups of K and Ca), I named *meta groups*. The number of any meta group corresponds to the highest possible valence which can be displayed by the elements of the same group.

The borderline between ortho and meta groups marks the beginning or the end of any series.

THE INTERRUPTIONS OF THE LONG PERIODS AND THEIR INTERPRETATION

In consequence of the insertion of the rare-earth metals into the system, we observe the gaps in the fourth, fifth, and seventh periods between the second and third meta groups. These gaps just correspond to the interruptions which take place in the normal building (stratification) of electronic shells. With the third meta group begins the abnormal structure which is observed in the whole third sector, so that the elements of this sector, which in Bohr's table are placed in a single frame, are exactly the same as in his classification. Finally, the rare-earth metals, which occupy the place between the second and third meta groups, are twice-abnormal, and are just those elements which in Bohr's table (lanthanum excepted) are placed in a double frame.

THE POSITION OF HYDROGEN IN THE SYSTEM

Since hydrogen is like an ingredient of all other elements (see Prout's hypothesis), it is placed high, *i. e.*, on the vertex of the cone. Nevertheless, in order to show the connection of hydrogen with the groups of alkaline metals and of halogens* (for it possesses metallic as well as metalloid properties) the contours of letter-inscription of the symbol H are placed above both lithium and fluorine.

THE POSITIONS OF LITHIUM AND SODIUM

Including all elements of short periods in the fourth sector emphasizes the normality of their structure; an incongruity exists, however, in lithium and sodium that are separated from alkaline metals and beryllium and magnesium, alkaline-earth metals.

Certainly lithium and sodium which, like potassium, rubidium, and cesium, follow noble gases and are the beginning of periods, will have properties more like those of potassium, rubidium, and cesium than those of copper, silver, and gold, which are placed in the middles of periods, far from the noble gases.

On the other hand, however, it is impossible to consider lithium and sodium as complete analogs of potassium, rubidium, and cesium.

"Sodium, and especially lithium salts, as regards many of their properties are incomparable with the salts of potassium, rubidium, and cesium."[11]

The difference in these elements is particularly noticeable in the phenomenon of isomorphism. Metallic potassium and sodium, as well as the majority of their compounds, are not isomorphous. Besides, many salts of sodium, unlike those of potassium, crystallize in the form of hydrates. For example:

Hydrates: $Na_2SO_4 \cdot 10H_2O$; $Na_2CO_3 \cdot 10H_2O$; $Na_2HPO_4 \cdot 12H_2O$
Anhydrous salts: K_2SO_4; K_2CO_3; K_2HPO_4.

Many salts of lithium (carbonate, phosphate, fluoride) differ from salts of other alkaline metals in their slight solubility. Further, lithium, unlike other alkaline metals, does not enter into the composition of any alum. Finally, while the elements of the potassium group give polyhaloid compounds of the RI_3 type, the corresponding compounds of sodium and lithium are unknown.

After these differences of lithium and sodium from the metals of the potassium group have been indicated, it is possible to find a resemblance of the first elements to those of the copper subgroup.

For instance, sodium gives the series of compounds isomorphous with the silver compounds:

$NaNO_3$	and	$AgNO_3$
Na_2SO_4	and	Ag_2SO_4
$Na_2S_2O_6 \cdot 2H_2O$	and	$Ag_2S_2O_6 \cdot 2H_2O$

When considering the strong bases of alkaline metals as one of their particularly characteristic properties, we must not forget that silver oxide represents a rather strong base too.

Generally, it is possible to say that the introduction of lithium and sodium into the same group with copper, silver, and gold is as logical as joining nitrogen, phosphorus, arsenic, antimony, and bismuth in one group: that does not call forth any objection, notwithstanding the sharp difference between physical and chemical properties of the elements of the last group.

When Mendeléeff arranged the elements in a long-periodic table in his "Principles of Chemistry," (Russian seventh edition, 1903), he put lithium and sodium into one line with copper, silver, and gold. Finally, such an eminent teacher as Alexander Smith, in his textbook of chemistry, studied lithium and sodium separately from potassium, rubidium, and cesium.

THE DISPOSITION OF BERYLLIUM AND MAGNESIUM

I consider that there must be still less objection to the setting of beryllium and magnesium above zinc, though at present they are often joined with the group of alkaline-earth metals (calcium, strontium, and barium). Antropoff, analyzing the question of where beryllium and magnesium must be placed, says, "Es kommt darauf an, welche Eigenschaften man vergleicht und in den Vordergrund stellt."[12]

So, for example, while magnesium and zinc are isomorphous (in spinels) and reveal the same coördinative number (in sulfates with seven molecules of water of

* Like metals, hydrogen can displace other metals from their salts; for instance, copper from copper salts at high pressure. Like halogens, hydrogen with metals gives salts (hydrides), displaying the negative valence of one (−1).

[11] F. EPHRAIM, "Inorganic chemistry," Leningrad, 1932, Part I, p. 202 (Russian edition).

[12] H. VON ANTROPOFF UND M. VON STACKELBERG, "Atlas der physikalischen und anorganischen Chemie," Verlag Chemie, Berlin, 1929, p. 18.

crystallization), that cannot be said about calcium; on the other hand, according to analytical reactions magnesium is nearer to calcium than to zinc, etc. In my table beryllium and magnesium are placed above zinc, as in the Werner-Pfeiffer table.[13]

THE POSITION OF BORON AND ALUMINUM IN P. S. E.

As to boron and aluminum, which have normal structure, I see no sufficient reason for transferring them into the scandium group, where the elements with abnormal structure have found their place.

THE COMPOSITION OF GROUPS AND SIMILARITY OF ORTHO AND META GROUPS

Thus my table, adjoining the long-periodic type and based on the structure of the atom, arranges into groups only the elements which are similar in their properties. Certainly, there are many similarities in the elements of the ortho and meta groups, which have the same numbers. The exceptions are the elements of the two divisions of the eighth group.

THE BORDER BETWEEN METALS AND NON-METALS

As may be seen from my table, one can draw on it precisely the border (die Grenze) between metals and non-metals according to their physical and chemical properites.* That is very important from the methodical point of view; to trace such a border on the usual Mendeléeff table is impossible.

THE COLORS OF IONS; MAGNETIC PROPERTIES

Concerning the elements which give colored ions and possess paramagnetic properties, one may stress the fact that they are concentrated for the most part in the third large sector of the table, where, as we have seen, the elements with abnormal structures have found their place.†

The elements of the fourth sector, which have normal structures, are diamagnetic and give colorless ions.‡ Therefore, the magnetic properties and the colors of ions may be related to the structures of the electronic shells of atoms.

SUMMARY

Summarizing the chief features and advantages inherent, in my opinion, in the new form of P. S. E. composed by me in 1930** and described in this paper, one can record the following conclusions:

1. The table graphically reflects the process of the construction of electronic shells of atoms, pointing out the places where it takes place normally, where abnormally, and in what degree; the table shows this so exactly that while looking at it one can copy out the arrangement of electrons in each quantum group.

2. Each separate group unites the elements which are in close natural relationship, thus facilitating the learning and memorizing of the composition of groups. In order to point out the relationships, it is not necessary to use indicating lines, as it is in the tables of Bohr,[14] Antropoff,[15] and Clark.[16]

3. The rare-earth metals have found a logical place in the table, and their inclusion there is correlated with the change of the process of construction of electronic shells.

4. In the table are clearly indicated the borders: (*a*) between the series of elements, (*b*) between metals and non-metals.

5. The location of elements which possess paramagnetic properties and give colored ions is shown.

6. Superficial indices show the maximum positive and negative valences of elements and their physical states.†

I believe that the graphical representation of Mendeléeff's periodic law which I have described will be useful in the study of inorganic chemistry, as a rationally constructed diagram and as a kind of work instrument which reveals the most important properties of chemical elements and the order of their change in connection with the structure of atoms and with the change of atomic number.

[13] A. WERNER, *Ber.*, **38**, 914 (1905); P. PFEIFFER, *Naturwissenschaften*, **8**, 991 (1920).

* The border between metals and non-metals is marked on the table in the form of a stepped (treppenartig) line, passing through the fourth large sector.

† The elements giving colored ions are marked on the table with black dots over the symbols.

‡ Copper and gold, which are in the fourth sector, give colored ions only when they show, so to speak, the abnormal valence, *i. e.*, greater than the number of the group to which they belong; but the ions of monovalent copper and gold must be colorless or pale yellow, to judge from the color of copper chloride and gold chloride.

** After I had used the table in my classes for four years it was printed in 1934 by the White-Russian State Publishing House, Minsk.

[14] N. BOHR, *loc. cit.*, p. 9.

[15] A. VON ANTROPOFF AND A. VON STACKELBER, Atlas, Figure 1.

[16] J. D. CLARK, *loc. cit.*, p. 675.

† Gaseous bodies have symbols which are drafted with dots; liquids have horizontal shading; solids are denoted by entire black letters; rare-earth metals have vertical shading.

STUDYING CHEMISTRY IN SUMMER WITH COMFORT

Micro-Qualitative Analysis, Chemical Microscopy, General Chemistry, and Elementary Organic Chemistry, as well as courses in other departments, may be studied this summer under cool and comfortable temperature conditions. These courses together with research in these fields and in Electrochemistry will be offered to properly qualified students at the University of Maine. The woods, lakes, and sea coast of the state present opportunities for pleasant week end trips. The session begins July 6th and lasts for six weeks. For further details address Professor Carl Otto, Chemistry Department, or Professor Chas. Dickinson, Acting Director of the Summer Session, University of Maine, Orono, Maine.

COLD LIGHT BROUGHT INTO THE CLASSROOM

EVANS W. COTTMAN

Madison, Indiana

IN PRACTICALLY all elementary courses in chemistry much space is allotted to the study of heat energy released during chemical reactions. However, very few people realize that many chemical reactions produce *light* without producing perceptible heat. Such reactions may be termed chemiluminescent reactions, and the light so produced may be properly termed "cold light." Usually, the amount of light in such reactions is very small, but it may be considerable in some instances, as in the case of the firefly.

In the March, 1934, issue of THIS JOURNAL E. H. Huntress, L. M. Stanley, and A. S. Parker presented an article describing the preparation and properties of the recently discovered 3-aminophthalhydrazide. This compound gives the most brilliant example of chemiluminescence so far discovered. However, it is somewhat difficult and expensive to prepare.

The following article outlines a few experiments in chemiluminescence which, if not so brilliant, may be performed easily, in any small laboratory equipped with a dark room.

Oxidation of Lophine.—For any laboratory possessing a small amount of benzaldehyde, this is a most satisfactory reaction as regards simplicity of preparation and production of light.

Crude lophine (triphenylglyoxaline) is easily prepared as follows: twenty-five cc. of benzaldehyde is shaken well with 100 cc. of ammonium hydroxide, and the mixture is allowed to stand in a stoppered flask for three days. A white cake of hydrobenzamide forms. This cake is broken up, washed with water, then with alcohol, and is placed in an evaporating dish. It is then heated and stirred constantly until it becomes a dark brown liquid. Then it is allowed to cool. It hardens to a glassy-looking mass. This is crude lophine. From the standpoint of light production it is unnecessary to attempt further purification of the lophine.

The reagents are then prepared as follows.

A. Lophine Solution.—About 2 g. of the crude lophine dissolved in 100 cc. of alcohol (methyl or ethyl alcohol or acetone may be used).

B. Hydrogen Peroxide Solution.—Ten cc. of the commercial 3 per cent. hydrogen peroxide solution is added to 90 cc. of ethyl or methyl alcohol.

C. Alcoholic Potash Solution.—Five g. of potassium hydroxide is dissolved in 75 cc. of water, and 25 cc. of alcohol is added.

D. Sodium Hypochlorite Solution.—The commercial cleaning fluid "Clorox" may be used. To make up this solution 10 cc. of Clorox is added to 90 cc. of water.

To produce chemiluminescence place 10 cc. of solution *A* in a beaker, then add 25 cc. of solution *B*, and 20 cc. of solution *C*. In a second beaker place 25 cc. of solution *D*. The room is darkened, and the contents of the first beaker are poured into those of the second beaker. A beautiful yellow luminescence will immediately occur.

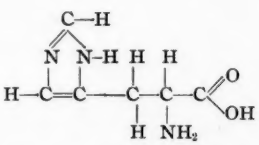
OTHER LUMINESCENT SUBSTANCES

While lophine luminescence is more intense, many other substances of much more common occurrence will also give light and may be substituted for the lophine. The same reagents that were described previously may be used (in the same proportions) except that these other substances may be substituted in place of the lophine.

The following substances have been found to be luminescent in alkaline solution upon oxidation with Clorox and hydrogen peroxide: coffee, cayene pepper, black pepper, tea, cocoa, ginger, yeast, mustard, and urine. Either a hot-water or an alcohol extraction of these substances may be used. In repeating the experiments with these substances, it is well to remember that the intensity of the light is very small. Therefore, the eyes must be thoroughly adapted to dark before performing the experiment. A number of carbohydrates have also been tried. They gave no light themselves. The carbohydrates were then heated or fused and the new samples were tried. After this treatment they were, without exception, luminescent.

BRIEF DISCUSSION OF LUMINESCENCE

The writer's experience in the field of chemiluminescence has led him to believe that the phenomenon is generally one of oxidation in which certain types of ring compounds are disrupted. The accompanying electronic disturbances are such as will produce a visible spectrum. Repeated experiments have led to the conclusion that the disruption of the glyoxaline ring is singularly fitted for producing chemiluminescence. Many naturally occurring proteins contain the amino acid, histidine, which contains the glyoxaline ring



Histidine itself is luminescent when oxidized, and it would seem possible that the presence of this radical might well account for some of the luminescence observed in naturally occurring substances. Obviously, this is only one of the luminescent groups. The exact nature of the luminescent carbohydrate groups can at present be only a matter of guesswork. Some oxidations of a simpler nature have been found to be slightly luminescent. For example, whenever sodium hypochlorate is added to hydrogen peroxide in alkaline solution, a faint flash of light occurs.

IS THE HUMAN BODY POTENTIALLY CAPABLE OF LUMINESCENCE?

The answer would seem to be in the affirmative. The writer has produced light by oxidizing urine with hemoglobin in an alkaline medium in the presence of a peroxide. All the ingredients necessary for light production are undoubtedly present in the human body, although normally these would not be brought together. However, it is quite possible to conceive that this might occur abnormally, with resulting luminescence. This idea is suggested as a possible explanation for the luminosity occasionally reported occurring in certain individuals.

EMIL ABDERHALDEN*

NO CONTEMPORARY biochemist is better known than the editor of the "Handbuch der biologischen Arbeitsmethoden." However, Emil Abderhalden's enviable reputation is not primarily derived from his efficient leadership in this monumental production; rather, his recognized eminence has been attained through the constant stream of high-class experimental studies that has flowed from his laboratory. His researches have covered or touched so many areas of his chosen field that an abstract of his hundreds of published papers might almost serve as a syllabus of a comprehensive course in physiological chemistry.

Though a choice is difficult, the following will give an idea of the variety of his scientific output. By comparative analyses of bloods he has shown that the serum contains about the same content of mineral matters, no matter how widely varied were the animal species studied, a fact of importance in the planning of diets. On the other hand, the corpuscles differ markedly in this respect. He has made extensive studies of the mineral content of milks and sought to correlate the findings with the growth rate of the new-born animals. The resorption and assimilation of iron and the effect of living at high altitudes on the formation of blood are other typical examples of the topics that interested him in the early part of his career.

His work on proteins is outstanding. He has shown that, by and large, the various albumins contain the same amino acids. He found that proteins are extensively degraded in the gastro-intestinal tract, but that the animal organism can elaborate albumin from amino acids. This latter fact was utilized in studying the biological activity of the individual amino acids, by noting the influence of diets from which the acid under consideration had been omitted. He showed that amino acids are always present in the blood. He has synthesized numerous polypeptides, has isolated some of these from protein and demonstrated the identity of the natural and synthetic product. He has employed polypeptides as substrates in his studies directed toward the elucidation of the action of the polypeptidases.

His discovery of the protective ferments opened up a field that has engaged the attention of many workers. He showed that parenteral introduction of albumin was followed by the appearance in the blood plasma and urine of proteinases which are highly specific in that they are capable of degrading only the injected albumin. He applied protective ferments to the study of heredity and transmission; he showed that protective enzymes that can break down placental proteins are present during pregnancy. He has worked out a reaction for the detection of pregnancy and has developed a procedure for the diagnosis of cancer. He discovered new structural units of protein, norleucine, and norvaline. He has studied protein metabolism and investigated the origin of creatine. He has shown that glycocoll can protect easily oxidizable materials.

Hormones and vitamins form a further chapter in his researches. He has studied the influence of vitamin B_1 on carbohydrate metabolism and has shown that the demand for this food accessory is dependent on the extent of the metabolism. The functions of vitamin C have also been of special interest to him.

He is corresponding or honorary member of about fifty scientific societies and academies. He is now President of the Deutschen Akademie der Naturforscher. Of his numerous honors, he is particularly proud of the Berzelius Medal conferred on him by the Swedish Society of Physicians, a distinction hitherto received only by his revered teacher, Emil Fischer.

Emil Abderhalden was born in Switzerland on March 9, 1877. He received his medical degree in 1901 from the University of Basel. He then went to the University of Berlin, where he occupied various teaching posts until 1911, when he was called to the University of Halle as Director of the Physiological Institute, where he has preferred to remain, despite flattering offers from other universities.

(*Contributed by Ralph E. Oesper, University of Cincinnati*).

* See frontispiece.

THE PRUSSIAN BLUE PARADOX

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The reactions between ferric and ferrocyanide ions to form Prussian blue and of ferrous and ferricyanide ions to form Turnbull's blue are profoundly influenced by the occurrence of the ionic redox equilibrium: $Fe^{+++} + [Fe(CN)_6]^{\equiv} \rightleftharpoons Fe^{++} + [Fe(CN)_6]^{=}$, *which is largely displaced toward the right.*

✦ ✦ ✦ ✦ ✦ ✦

INTRODUCTION

THE action of ferric ion on ferrocyanide ion results in the production of blue substances bearing the generic name Prussian blue. When an excess of ferric ion is employed, the product has the formula $Fe_4[Fe(CN)_6]_3$ and is known as insoluble Prussian blue. From equimolecular quantities of ferric and ferrocyanide ions, a product is formed which contains the metallic ion of the soluble ferrocyanide employed. Thus, with potassium ferrocyanide, for example, the blue product has the formula $KFe[Fe(CN)_6]$ and is known as soluble Prussian blue. The term soluble is a misnomer, however, and refers not to the true solubility of the product (it is actually insoluble in water) but to the ease with which it forms colloidal solutions.

Although it would appear from the formulas given above that the formation of Prussian blue involves simply the mutual precipitation of ferric and ferrocyanide ions, and should, therefore, be an instantaneous reaction, it has actually been found to be a relatively slow reaction.[1] It might be anticipated, however, that excess of ferric ion would accelerate the formation of Prussian blue. Actually, the opposite is found to be the case. *Excess of ferric ion hinders the formation of Prussian blue.*

To account for the slowness of Prussian blue formation, Vorländer took refuge in the labyrinths of colloid chemistry. He contended that ferric salt solutions were to be considered incomplete colloids whose particles had a size between that of true solutions and those visible in the ultramicroscope. Hence, the slow reaction with ferrocyanide ion. The results obtained in the present paper make it appear that this explanation is invalid and that the elucidation of the Prussian blue paradox lies in the redox reaction:

$$Fe^{+++} + [Fe(CN)_6]^{\equiv} \rightleftharpoons Fe^{++} + [Fe(CN)_6]^{=}$$

A DEMONSTRATION

It is a simple matter to show that the formation of Prussian blue is a slow reaction. On mixing equal volumes, say 50 cc. of 0.0002 formal $K_4Fe(CN)_6 \cdot 3H_2O$ (in water) and 0.0002 formal ferric alum, $NH_4Fe(SO_4)_2 \cdot 12H_2O$ (in tenth-formal $KHSO_4$)* the originally colorless liquids form a yellow solution which quickly alters to green and finally to blue within one minute. If the solutions taken are three times as strong (0.0006 formal) the succession of colors is complete within one second while, if the solutions are only one-third as strong as the original solutions (0.00007 formal), the reaction requires the better part of an hour.

THE REDOX EQUILIBRIUM

A finite time is thus seen to elapse between the mixing of ferric and ferrocyanide ions and the appearance of Prussian blue. It may now be worth while to consider the possibility of an oxidation-reduction reaction between these ions in solution *preceding* the formation of Prussian blue.

A mixture of ferric and ferrous ions forms a reversible redox system which imparts a definite potential to an inert electrode such as platinum, as does, likewise, a mixture of ferro- and ferricyanide ions. From the single electrode potentials of these systems one may predict the following equilibrium:

$$Fe^{+++} + [Fe(CN)_6]^{\equiv} \rightleftharpoons Fe^{++} + [Fe(CN)_6]^{=}[2]$$

and calculate the equilibrium constant:

$$K_{298} = \frac{[Fe^{++}][[Fe(CN)_6]^{=}]}{[Fe^{+++}][[Fe(CN)_6]^{\equiv}]} = 100{,}000 \text{ (approx.)}[3]$$

The size of the equilibrium constant indicates that the reversible reaction is largely displaced toward the right. In other words, when ferric ion is added to an equimolecular quantity of ferrocyanide ion, an oxidation-reduction occurs in which *the ferric ion is almost completely reduced to ferrous ion by the ferrocyanide ion which is simultaneously oxidized to ferricyanide ion.*

[1] D. Vorländer, *Ber.*, **46**, 181 (1913); *Kolloid-Z.*, **22**, 103 (1918).

* These dilute solutions are conveniently prepared by diluting 1 cc. of 0.01 formal solutions to 50 cc. For ferrocyanide ion dissolve 0.422 g. of $K_4Fe(CN)_6 \cdot 3H_2O$ in 100 cc. of water. For ferric ion dissolve 0.482 g. of ferric alum, $NH_4Fe(SO_4)_2 \cdot 12H_2O$ in 100 cc. of tenth-formal $KHSO_4$. The bisulfate serves to prevent hydrolysis of the ferric salt. (A perfectly colorless solution is obtained.) Dilutions of the ferric alum solution are made with tenth-formal $KHSO_4$. The ferrocyanide solution should be freshly prepared.

[2] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York City, **1923**, p. 396.

[3] E. Müller and T. Stanisch, *J. prakt. Chem.*, (2) **79**, 81 (1909). These authors employed 0.71 v. and 0.41 v. for the respective potentials. The current values of 0.75 v. and 0.49 v. yield a value closer to 20,000 for K_{298}. The actual value is not significant for the present discussion as long as it is large.

Thus, for example, if 1.0 mole of ferric ion is treated with 1.0 mole of ferrocyanide ion, it may be calculated that, at equilibrium, 0.9968 mole of ferrous and ferricyanide ions will have been formed and only 0.0032 mole of each of the original ions will remain.

	Fe^{+++} +	$[Fe(CN)_6]^{\equiv}$	$\rightleftharpoons Fe^{++}$ +	$[Fe(CN)_6]^{=}$
Start with	1.0	1.0	0	0
At equilibrium	$(1-x)$	$(1-x)$	x	x

$$\frac{x^2}{(1-x)^2} = 100{,}000$$

$$x = 0.9968$$

It is now conceivable that any or all of the possible combinations of the ions that participate in the redox equilibrium may precipitate. If it is assumed, as seems likely, that it is the ferric and ferrocyanide ions which are actually involved in the formation of Prussian blue, then it becomes clear that *the formation of Prussian blue is slow because the ions required for it practically disappear when mixed*, owing to the redox reaction which they undergo instantaneously. Of course, as the small amounts of ferric and ferrocyanide ions remaining combine to form Prussian blue, the redox equilibrium is continuously disturbed and the originally formed ferrous and ferricyanide ions gradually regenerate the reciprocal pair, thus:

Prussian Blue

$$Fe^{+++} + [Fe(CN)_6]^{\equiv} \overset{\text{fast}}{\rightleftharpoons} Fe^{++} + [Fe(CN)_6]^{=}$$
$$\downarrow \text{slow}$$

FURTHER DEMONSTRATIONS

In the previous demonstration it was shown that the time required for the appearance of Prussian blue depends upon the concentration of the reacting ions. It is possible, therefore, by choosing a suitable concentration, to study the redox reaction experimentally before the formation of Prussian blue interferes. For this purpose, 0.0001 *M* solutions, which give a blue color in a period of time varying from fifteen to thirty minutes, are convenient. Fifty cc. of 0.0001 *M* ferric ion is placed in each of two 150-cc. beakers. To the first beaker is now added 50 cc. of distilled water, while to the second is added 50 cc. of 0.0001 *M* ferrocyanide ion. Ferric ion is now tested for in both beakers by adding 5 cc. of *M* KSCN. A positive test is obtained in the first, while the second gives a negative result. This indicates that ferrocyanide ion reduces ferric ion, thereby causing the practical disappearance of both of these ions according to the equation given above. That ferricyanide is formed is indicated by the yellow color obtained immediately on mixing the colorless ferric and ferrocyanide ions. The presence of ferricyanide may be confirmed by testing for it with ferrous ion. Thus, a few cc. of 0.01 *M* ferrous ion added to the second beaker cause an immediate blue color (Turnbull's blue).

To test the action of excess of either of the reagents on the formation of Prussian blue, 150 cc. of 0.0001 *M* ferric ion is mixed with 150 cc. of 0.0001 *M* ferrocyanide solution and the mixture divided among three beakers. The first is kept as a control. A few cc. of 0.01 *M* ferric ion is added to the second beaker, while a few cc. of 0.01 *M* ferrocyanide ion is added to the third. A blue color appears immediately in the third beaker, slowly in the control, and still more slowly in the second beaker. That is to say, while excess of ferrocyanide ion has the expected accelerating effect on the formation of Prussian blue, excess of ferric ion has just the opposite effect; namely, it actually hinders the formation of the blue.

FURTHER THEORY

In considering the explanation of this paradox, it should be kept in mind that Prussian blue is not formed instantaneously, but only after the establishment of the redox equilibrium at the expense of the ferric and ferrocyanide ions. What effect will excess of ferric ion have upon this equilibrium? It has been calculated previously that the equimolar quantities of ferric and ferrocyanide ions are reduced to 0.0032 of their original values by the oxidation-reduction reaction. If a similar calculation is made for the action of an excess (say, tenfold) of ferric ion on one mole of ferrocyanide ion:

	Fe^{+++} +	$[Fe(CN)_6]^{\equiv}$	$\rightleftharpoons Fe^{++}$ +	$[Fe(CN)_6]^{=}$
Start with	10	1	0	0
At equilibrium	$(10-x)$	$(1-x)$	x	x

$$\frac{x^2}{(10-x)(1-x)} = 100{,}000$$

$$x = 0.9999909$$
$$(1-x) = 0.0000011$$
$$(10-x) = 9.0000011$$

it is found that the excess of ferric ion simply shifts the redox equilibrium toward the right and reduces the ferrocyanide ion to 0.0000011 of its original value or to 0.00034 of its value in the presence of an equimolar quantity of ferric ion. Actually, the ion product, $[Fe^{+++}]$ $[[Fe(CN)_6]^{\equiv}]$, remains practically constant, and the expected effect of excess of ferric ion on the formation of Prussian blue is nullified by the enormous reduction in ferrocyanide ion which it occasions.

Now, excess of ferrocyanide ion should have exactly the same effect upon ferric ion that has just been found for excess of ferric ion on ferrocyanide. In the demonstration, however, excess of ferrocyanide was found to be effective in hastening the formation of Prussian blue. How is this fact to be reconciled with what has gone before? Calculation leads to the following results.

	Fe^{+++} +	$[Fe(CN)_6^{\equiv}]$	$\rightleftharpoons Fe^{++}$ +	$[Fe(CN)_6]^{=}$
Start with	1	10	0	0
At equilibrium	0.0000011	0.0000011	0.9999909	0.9999909

That is, here the *ferric ion* is reduced to 0.0000011 of its original value. The ion product $[Fe^{+++}]$ $[[Fe(CN)_6^{\equiv}]]$ again remains practically constant. It must now be recalled that any of the four possible oppositely-charged pairs of the four ions involved in the redox equilibrium may be precipitated. Of these, *ferrous ferrocyanide* is known to be insoluble. It is well, therefore, to consider the ion-product $[Fe^{++}]$ [[Fe

$(CN)_6]^{\equiv}$] which prevails after the establishment of the redox equilibrium in the various mixtures of ferric and ferrocyanide ions for which calculations have been made.

Start with $[Fe^{+++}]$	$[[Fe(CN)_6^{\equiv}]]$	$[Fe^{++}][[Fe(CN)_6]^{\equiv}]$ *at equilibrium*
1	1	0.0032
10	1	0.0000011
1	10	9.0

From this table it is seen that in the presence of excess of ferrocyanide ion the ion product $[Fe^{++}]$ [[Fe $CN)_6]^{\equiv}$] is greatly increased, and hence the formation of ferrous ferrocyanide is favored. Once formed, the colorless ferrous ferrocyanide may be oxidized to Prussian blue by the air or by the ferric ferricyanide remaining in solution.

SOLUBLE TURNBULL'S BLUE

Thus far it has been demonstrated that an immediate redox equilibrium is established when ferric and ferrocyanide ions are mixed, resulting in their nearly complete conversion to ferrous and ferricyanide ions, as a consequence of which the assumed formation of Prussian blue from the original pair of ions is slow. Now it is a criterion of true equilibrium that the same final state may be approached from both sides of the reversible reaction. It may, therefore, be anticipated that if equimolar quantities of ferrous and ferricyanide ions are mixed they will react to a slight extent to form ferric and ferrocyanide ions in order to satisfy the equilibrium constant, and the same equilibrium concentrations of the four ions involved will result as when equimolar quantities of ferric and ferrocyanide ions are employed as reagents. Hence, whatever blue product is formed in the first case should be formed here also and at the same rate. That the product obtained from equimolar quantities of ferrous and ferricyanide ions is the same as that from equimolar quantities of ferric and ferrocyanide ions was considered by Skraup as early as 1877[4] and was established by potentiometric methods by Müller and Lauterbach in 1922.[5] Vorländer, on the other hand, claimed that unlike the formation of a blue from ferric and ferrocyanide salts, which is slow, the production of a blue from ferrous and ferricyanide ion is instantaneous.

SOME FINAL DEMONSTRATIONS

Paralleling the previous experiments with mixtures of ferric and ferrocyanide ions, 50-cc. portions of 0.0006, 0.0002, and 0.00007 formal solutions of $K_3Fe(CN)_6$ (in water) are mixed with like concentrations of Mohr's salt, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (in tenth-formal $KHSO_4$). The results are indistinguishable from those obtained with the reciprocal pair of ions, the originally yellow (due to ferricyanide) mixtures turning green and finally blue in about a second, a minute, and an hour, respectively.

To study the effect of excess of ferrous on ferricyanide ions, 150 cc. of 0.0001 *M* ferrous ion is mixed with 150 cc. of 0.0001 *M* ferricyanide and the mixture divided among three beakers. The first is kept as a control, while a few cc. of 0.01 *M* ferrous ion is added to the second beaker, and a few cc. of 0.01 *N* ferricyanide ion to the third. A blue color appears at once in the second beaker, a green almost as quickly in the third, while the control requires about fifteen to thirty minutes to produce a blue color.

It thus appears that unlike the inhibiting action of excess ferric ion on ferrocyanide, excess of ferrous ion really favors the formation of a blue product from ferricyanide ion.*

A FINAL EXPLANATION

To account for the foregoing demonstrations it is necessary to return once more to the calculation of equilibrium conditions. If an excess, say, tenfold, of ferrous ion to one mole of ferricyanide ion is employed, the following result is obtained.

	Fe^{+++} +	$[Fe(CN)_6]^{\equiv}$ ⇌	Fe^{++} +	$[Fe(CN)_6]^{=}$
Start with	0	0	10	1
At equilibrium	0.010	0.010	9.990	0.990

If these figures are compared with the previous calculations, it will be seen that excess of ferrous ion, while having only a slight effect on the ferricyanide ion, causes a tripling of *both* the ferric ion and the ferrocyanide ion. (Contrast this with the effect of excess of ferric ion on ferrocyanide ion where the gain in ferric ion is compensated by a reciprocal loss in ferrocyanide.) Hence, the accelerating action of excess of ferrous ion on ferricyanide.

Similar figures are obtained for the effect of excess of ferricyanide ion on ferrous ion; for example:

	Fe^{+++} +	$[Fe(CN_6]^{\equiv}$ ⇌	Fe^{++} +	$[Fe(CN_6])^{=}$
Start with	0	0	1	10
At equilibrium	0.010	0.010	0.990	9.990

The green color obtained in this case is probably the mixed color of the soluble Prussian blue and the yellow ferricyanide which is present in excess.

AN APPLICATION TO QUALITATIVE ANALYSIS

The qualitative test for nitrogen in organic compounds frequently involves the detection of small amounts of ferrocyanide which is produced by the action of ferrous ion on the cyanide resulting from a sodium fusion. It is, therefore, desirable to take account of the ineffectiveness or even the hindrance of excess of ferric ion in producing Prussian blue. During the "nitrogen test" considerable ferric ion is produced by the aerial oxidation of ferrous hydroxide. Two methods of obviating this disadvantage have been

[4] Z. A. SKRAUP, *Ann.*, **186**, 371 (1877).
[5] E. MÜLLER AND H. LAUTERBACH, *J. prakt. Chem.*, (2) **104**, 241 (1922).

* It is strictly this difference in the effect of excess of ferrous and ferric ions on the corresponding complex ions which Vorländer (*loc. cit.*) observed when he wrote that one reaction (ferric ion and ferrocyanide) was slow and the other (ferrous ion and ferricyanide) instantaneous.

recommended, both on empirical bases. Vorländer suggests filtering the alkaline test mixture before acidification, thus separating the iron hydroxides from the ferrocyanide ion which appears in the filtrate. The filtrate is then acidified and treated with ferrous sulfate, the requisite ferric ion for Prussian blue formation being produced by aerial oxidation. Kamm[6] recommends the procedure of Viehoever and Johns[7] who add KF to the test mixture, although no explanation is offered for its use by these authors. It now appears that the function of the fluoride is to "tie up" the excess of ferric ion (produced by aerial oxidation) and to prevent the unfavorable shifting of the redox equilibrium (conversion of ferrocyanide to ferricyanide) by the ferric ion. It is curious that the lack of an explanation for the use of fluoride has led one author to recommend adding both ferric chloride and potassium fluoride to the nitrogen test. Certainly, the common practice of employing ferric chloride in this test is both unnecessary and undesirable.

[6] O. KAMM, "Qualitative organic analysis," 2nd ed., John Wiley & Sons, New York City, 1932, p. 135.
[7] A. VIEHOEVER AND C. O. JOHNS, *J. Am. Chem. Soc.*, **37**, 601 (1915).

ACKNOWLEDGMENT

The author is indebted to his former students, Messrs. A. Schwebel and H. Rosenwasser, for checking the experiments reported in this paper. They are now engaged in studying the behavior of other reversible redox systems of metallic ions, such as Cu^{++}—Cu^{+}, toward the ferrocyanide-ferricyanide system.

STANDARD MIXED CHLORIDE SAMPLES

THE EFFECT OF BALL MILL GRINDING AND MIXING ON THE ACTUAL ANALYSES AS COMPARED WITH CALCULATED VALUES

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INTRODUCTION

THE preparation of student samples for practice analyses, in case large classes are involved, is a difficult problem. If a number of individual students are to be given the same samples for analysis, the sample should be made for a single semester's use; otherwise such a series of samples soon discontinue to be "unknowns." For a single semester's use in a class of fifty to one hundred students ten separate samples may be sufficient. A second alternative is to provide separate samples for each student, or pair of students at the most, which for a large class requires a much larger number of samples. In the latter case the same samples can be used continuously over a succession of semesters and still remain "unknowns." In the first case the samples are made and analyzed in small gross lots just sufficient for the semester's needs. In the second case they may be made in larger lots and numbers, to provide for continued use. In either case the total number of analyses on the part of the instructor and assistants makes their preparation an arduous task. Either a few analyses must be made each semester, or a large number at less frequent intervals. The practice often followed is to prepare large quantities of a few samples and use them continuously from semester to semester until they have lost most of their value as "unknowns." To purchase student samples from various possible sources of supply soon mounts into considerable expense where large classes are involved.

The remedy for both the alternatives mentioned is obviously to provide a method for the synthesis of such samples as mixed chlorides of potassium and sodium. By a knowledge of the purity of the separate ingredients and the weight of each, the resulting analyses can be calculated. The remaining point to be determined is that the two components are thoroughly ground and mixed and that the resulting mixture is homogeneous in each case. The separate ingredients, potassium chloride and sodium chloride, can be purchased in pure form at a moderate price. The question of the proper method for ensuring homogeneity, following the customary ball mill grinding and mixing, is the unknown factor requiring special study. It is the object of the present discussion to describe a suitable procedure for the preparation of such synthetic mixtures and to compare the actual results obtained with those predicted by synthesis.

BALL MILL GRINDING AND MIXING OF THE MIXED CHLORIDES OF POTASSIUM AND SODIUM

If a dry mixture of 40-mesh sodium chloride and potassium chloride is ground in a dry ball mill for a period of one hour the mixture has been reduced to such a fine state of subdivision that it tends to cake on

the walls of the ball mill jar. A quart size Abbé ball mill jar half full of agate balls and containing a pound of the mixed chlorides is conveniently used in this case. After two and one-half hours rotation most all of the sample mixture is caked against the side walls and bottom of the ball mill jar, but not sufficiently to harden the cake thus formed. After three and one-half hours the whole of the sample is caked but may still be easily removed from the jar, and simple working with a large mortar and pestle quickly restores it to its proper free flowing and finely ground condition. The conditions resulting in the formation of the cake in the ball mill jar are not remedied by any known procedure. The phenomenon of caking is inherent with this mixture of reagents, as it is also with many other dry mixed components. Certain other mixtures such as portions of different ground feldspars do not cake in the ball mill, no matter what the period of grinding may be. The question then to be answered is whether or not the caking results after the sample has been reduced to such a degree of fineness as to guarantee homogeneity. If not the analysis of the resulting product will show non-uniformity. In case the attainment of uniformity precedes the caking phenomenon, the process of synthesizing such mixtures is much simplified. In the opposite case it would be necessary to grind each portion of potassium and sodium chlorides separately to pass a 100-mesh sieve and mix weighed quantities of such samples by other means. The former process, which is much more convenient, was found to be adequate.

EXPERIMENTAL PROCEDURE IN PROVING HOMOGENEITY

A sample of known weight of pure sodium chloride (40-mesh) was placed in a one-quart size Abbé ball mill jar half full of agate balls. A sample of pure potassium chloride (40-mesh), also of known weight, was added. The jar was closed and rotated in a motor driven revolving rack for a period of two hundred ten minutes. The ground caked sample was removed from the jar and the agate balls separated out. The sample was transferred to a mortar and lightly ground with the pestle to an easily prepared free flowing mixture of 100-mesh fineness or less. Samples were then taken for analysis by the Mohr method. The results obtained are compared with the calculated chlorine value and the agreement between individual determinations indicated a satisfactory condition of homogeneity, as well as close approximation to the calculated values. The results are shown in Table 1.

TABLE 1

AGREEMENT BETWEEN CALCULATED AND DETERMINED VALUES FOR MIXTURES OF KCl + NaCl

	NaCl g.	*KCl* g.	*Calc.* % Cl	*Found* % Cl	*Variation in Duplicates* % Cl	*Variation from Calculation* % Cl
1.	60.2114	40.0010	55.43	55.65	+0.06 to −0.09	+0.22
	.....	.....	...	55.59	+0.11 to −0.05	+0.16
2.	101.0490	80.7073	54.84	55.00	+0.03 to −0.01	+0.16
	.....	.....	...	54.89	+0.03 to −0.03	+0.05
3.	.....	.....	...	55.02	+0.02 to −0.02	+0.02
	.....	.....	...	54.90	+0.05 to −0.05	+0.01

Each horizontal row represents results from four separate analyses.

Sample Number 2, Table 1, was prepared by grinding each of the separate ingredients to pass a 100-mesh sieve and then mixed by repeated passage through a coarse sieve to mix to homogeneity followed by the analyses as given. The sample, Number 3, was then placed in the ball mill jar without the use of grinding balls and rotated several hours to determine the caking tendency. It was not apparent. The process of grinding and mixing in one operation, being more simple in practice, was applied in the subsequent preparation of samples. All three of the separate modifications of mixing shown in Table 1 show a satisfactory agreement in uniformity and in calculated values.

PREPARATION OF A SERIES OF STUDENT SAMPLES BY THE BALL MILL GRINDING AND MIXING PROCEDURE

A series of ten different mixtures of pure potassium and sodium chlorides were weighed in approximately one-pound lots. These were ground for two hundred ten minutes in one-quart Abbé ball mill jars half full of half-inch granite balls. The caked samples were then removed, the balls separated and the caked samples reduced to a free flowing mixture by a brief treatment in a large porcelain mortar. They were then analyzed by Mohr's method and the calculated values compared with actual analysis. The results are shown in Table 2.

TABLE 2

COMPARISON OF CALCULATED CHLORINE VALUES WITH ANALYZED VALUES FOR A SERIES OF KCl + NaCl MIXTURES

Sample No.	*KCl* %	*NaCl* %	*Chlorine Calculated* %	*Chlorine Found* %	*Difference* %
1	9.26	90.74	59.40	59.37	−0.03
2	15.79	84.21	58.62	58.47	−0.15
3	24.96	70.54	56.81	56.85	+0.04
4	33.72	66.28	56.23	56.07	−0.16
5	39.45	60.55	55.49	55.59	+0.10
6	42.56	57.44	55.05	54.85	−0.20
7	46.98	53.02	54.54	54.30	−0.24
8	48.76	51.24	54.31	54.03	−0.28
9	17.08	82.92	58.42	58.15	−0.27
10	25.31	74.69	57.34	57.17	−0.17
				Average	−0.15

From an examination of Table 2 it will be observed that the average difference between the calculated values and those found is within the range of analytical accuracy which would be expected. The results tend to be somewhat low which may have been caused by slightly impure starting products. The water content of NaCl and KCl not removed under 400°C. is of the order involved.[1] The possible range in values from such mixtures is 47.56 per cent. Cl for pure KCl and 60.65 per cent. Cl for pure sodium chloride. The methods outlined have probably been previously employed, but no records can be found of a systematic discussion of the results, or an estimation of the agreement between calculated and determined values cited.

[1] SMITH, STUBBLEFIELD, AND MIDDLETON, *Ind. Eng. Chem., Anal. Ed.*, **6**, 314 (1934).

SUBSCRIPTS *on the* CHEMIST'S TYPEWRITER

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University of California at Los Angeles, Los Angeles, California

IN TYPEWRITING, subscripts and exponents are usually made by rolling the platen slightly or by the installation of special small characters in place of the less used ones of the machine. The first method is laborious and tends to produce irregularities in the location of the offset characters. The second gives only a limited number of subscript characters and requires the abandonment of characters which might otherwise be useful.

The author has avoided the disadvantages of both of these methods by a device which may be described as a "partial shift." The partial shift is accomplished by the use of a single extra key which rides on the arm of the regular shift key of the typewriter board that is used in making the capital letters. This extra key has a stop, adjusted so that the shift of the typewriter carriage is made to only a slight extent. Any character made while the carriage is in this slightly shifted position appears in the subscript position instead of the character of the capital keyboard appearing in the normal position as would be the case if the carriage were shifted completely. The partial shift key is held down while the subscript is made, just as is the regular shift key when capitals are to be made.

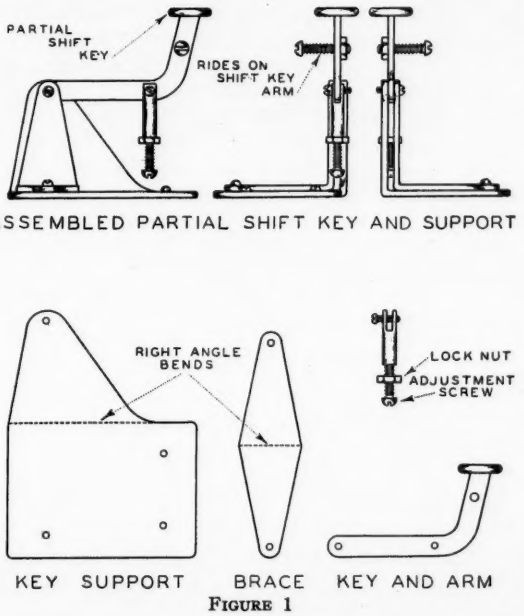

FIGURE 1

Two types of mountings for the partial shift have been used. The neatest type is that suitable for portable machines and others that are mounted on wooden bases. Figure 1 indicates how the partial shift attachment of this type was made and assembled.

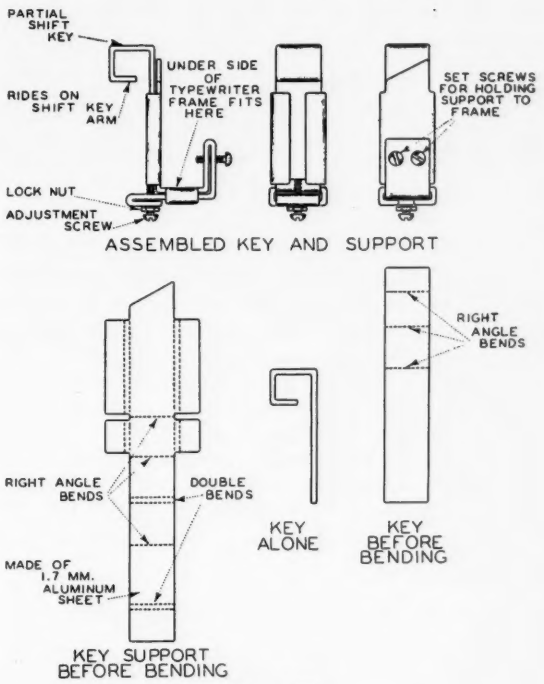

FIGURE 2

A typewriter key and arm were obtained from a typewriter repair shop. The key support and brace were cut from 3/4 by 3/4 inch angle brass. The holes were made with a No. 41 drill. The screw bolts and the tap used in making the threads were No. 4-40.

The attachment was placed on the base of the typewriter so that the rider bolt of the partial shift rested on the arm of the shift key on the right side of the machine. The partial shift key was placed in line with the second row of keys and the support attached to the wooden base of the typewriter with small wood screws.

The extent to which the subscripts are to appear

below the regular line is determined by a trial and error setting of the adjustment screw, after which the lock nut is tightened. On some typewriters the underline character, which is on the same key as the six, is so close to the number that there is only a narrow range of adjustment. Hence, the number six is a good character to use in the trial and error setting of the stop.

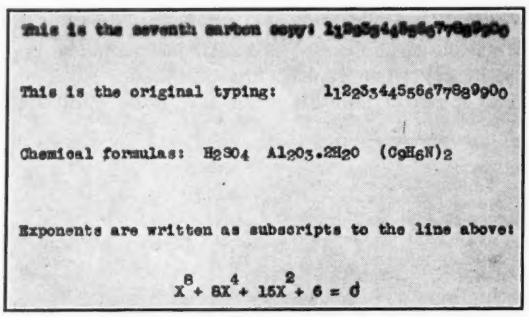
This is the seventh carbon copy: 1₁2₂3₃4₄5₅6₆7₇8₈9₉0₀
This is the original typing: 1₁2₂3₃4₄5₅6₆7₇8₈9₉0₀
Chemical formulas: H_2SO_4 $Al_2O_3.2H_2O$ $(C_9H_6N)_2$
Exponents are written as subscripts to the line above:
$X^8 + 8X^4 + 15X^2 + 6 = 0$

FIGURE 3

Figure 2 sets forth the construction and assembly of a partial shift attachment which was fastened to the frame of the machine rather than to the baseboard on which the machine was mounted. Exact dimensions are omitted, since it may be necessary to vary these slightly to suit the particular type of machine on which the attachment is to be used. Although this type of mounting is more conspicuous than the baseboard type it has been found to be quite satisfactory for use in writing subscripts.

The illustrations of Figure 3 show examples of the work done by the use of the attachment on the author's machine.

The advantages of the partial shift method of obtaining subscripts over the other methods which have been used are numerous.

(1) It is inexpensive to install.

(2) A large assortment of characters is made available for subscripts since all of the characters of the regular keyboard can be so used.

(3) The location of the subscript characters is adjustable and the position of the imprint can be duplicated exactly.

(4) The larger type for the characters made by this attachment yields clearer carbon copies than the smaller characters usually installed for this purpose.

(5) Since the subscripts are made from the keyboard, without adjustment of the platen, the method is a rapid one.

Doubtless the typewriter manufacturer would object to the compromise character of the device. Because of the curvature of the platen, the imprint of the partially shifted character is necessarily lighter at the bottom than at the top. This, however, cannot be detected by a casual inspection of the work done on the author's machine (see Figure 3). The fact that the carbon copy shows the partially shifted characters as clearly as the unshifted characters indicates that the curvature of the platen is of no great importance in this connection. The partially shifted carriage is not as well supported as the completely shifted one used in making the capitals. This is not desirable from a mechanical point of view. Nevertheless, the author has been unable to detect any disadvantage arising from lack of stability of the partially shifted carriage.

Students and colleagues of the author have used the device with much satisfaction. It has been tried successfully on three different models of the Royal typewriter, two models of the L. C. Smith, an Underwood, and a Remington machine.

REPORT OF THE CHAPEL HILL MEETING OF THE DIVISION OF CHEMICAL EDUCATION

The Chapel Hill meeting of the Division of Chemical Education of the A. C. S. was unusually successful. The attendance on several occasions exceeded the capacity of the room and considerable interest was shown in many of the papers. Three half-day sessions were occupied by the regular program and on the last afternoon an informal colloquium was held on the teaching of qualitative analysis. A number of the teaching problems in this field were discussed at length, and particular interest was shown in the use of semi-micro technique.

A special feature of note was the sound film on "Electrochemistry," the latest one of the series prepared at the University of Chicago.

The capacity of the dining room was taxed to the utmost for the luncheon. Professor H. N. Holmes, of Oberlin College, was the principal speaker, and other guests included the President of the Society, the President-Elect, and the Chairman of the Board of Directors. The assistant business manager reported optimistically on the financial state of the JOURNAL.

MINUTES OF THE EXECUTIVE COMMITTEE MEETING

The Executive Committee of the Division of Chemical Education met at Chapel Hill, N. C., on April 12, 1937. Present: O. M. Smith, Chairman; N. W. Rakestraw; Virginia Bartow; E. W. Phelan.

The following resolution was passed:

"Whereas, by the death of Louis W. Mattern, the Division has lost one of its staunchest and most loyal members, who for many years has maintained a most active interest in the field of chemical education,

Be it resolved, that the Division enter upon its minutes an expression of its sorrow and deep regret."

The question of establishment of a committee on student prize awards was referred to the Committee on Naming and Scope of Committees.

It was voted that regular yearly appropriations be made as follows:

For the Office of the Chairman	$25
For the Office of the Secretary	50
For the Office of the Treasurer	15

An informal report was received from the Treasurer, showing a balance of $479.65, the regular annual report to be made at the next meeting.

N. W. RAKESTRAW, *Secretary*

W. O. Brooks
A. T. Burtsell
R. K. Carleton
Tenney L. Davis
J. Howard Graham
B. Clifford Hendricks
J. W. Howard

ABSTRACTS

R. A. Baker, *Abstract Editor*

D. C. Lichtenwalner
Greta Oppe

C. M. Pruitt
Leopold Scheflan
A. A. Vernon
E. D. Walter
Mary Elvira Weeks
Sidney Weinhouse
G. H. Woollett

KEEPING UP WITH CHEMISTRY

The formation of crystals caused by the conditions of the phases. O. Gabran. *Wasserkraft und Wasserwirtschaft.*, **31**, No. 23, 301–2 (Dec. 1, 1936).—As observations of different ice crystal formations have shown that the crystalline structure depended on the condition of the vapor phase in the water, it seemed plausible that the crystals of other substances might also be influenced by the condition of the phases. The following physical phenomena supported this view, water droplets which are free from air can be greatly supercooled and superheated in oil; also when air is introduced into superheated water the latter evaporates with explosion-like velocity. It is furthermore known that the boiling point is influenced by the structure of the walls of a vessel and the air contents.

Experiments were carried out in which the vapor phase and its components were excluded as much as possible by melting and boiling the compounds under test under paraffin oil. As this oil represents one phase and one component, its presence does not vary the number of degrees of freedom. Crystallizations carried out simultaneously in the presence of air and after boiling in oil showed a decided difference in the crystalline form. Such differences were found with salicylic acid, salol, and menthol, sulfur, and resorcinol-calcium chloride.

As all the materials examined showed differences in their crystalline structure when frozen under the two sets of conditions, it is not impossible that metals may show some differences in their crystalline structure after the removal of the vapor phase from the melt. L. S.

Trends in wood pulp industry. H. R. Murdock. *Chem. & Met. Eng.*, **44**, 4–8 (Jan., 1937).—Three major conditions, namely, the depression with its buyers' market, the demand of the rayon industry, and the statistical position of wood pulp have given the wood pulp industry a healthy stimulus to forge ahead.

Technical developments are being advanced from all quarters, and this paper discusses some of the more outstanding cases.

Artificial stones made from alundum or from silicon carbide are replacing natural sandstones in the grinding machines. A numerically expressed fiber analysis has taken the place of the older method which depended on the operator's eye.

Three developments stand out as leading events in the progress of the sulfite process, namely, improved methods of burning sulfur and preparing the cooking liquor, the adoption of corrosion-resistant metals for digester construction and the preheating and fortifying of the liquor with relief gases before introducing the cooking solution into the digester. Much attention has been given to the method of discharging the digester and to the recovery of heat from the blow.

New bleaching processes have originated in many quarters. Most of these are based on the use of chlorine in combination with other chemicals. Due to the fact that short fibers do not contribute favorably to the strength of the pulp, methods of eliminating them are being worked out.

The modern pulp mill now employs three to four times as many technical men as it did five years ago. J. W. H.

A new material: ethyl cellulose. J. M. DeBell. *Chem. & Met. Eng.*, **44**, 31–2 (Jan., 1937).—Ethyl cellulose is the ether of cellulose and ethanol. It is marketed as a white granular powder. It is made by the action of ethyl chloride or ethyl sulfate on alkali cellulose. Its chief characteristics are toughness, low flammability, heat stability, light stability, extraordinary flexibility, thermoplasticity, extensibility, inertness to alkalis and dilute acids, excellent miscibility with oils, waxes, and resins, and solubility in low cost solvents.

With variation in ethoxy content its properties can be widely varied. It has found use as a thermoplastic adhesive for transparent material, as a bodying material in heat transfers to textiles (pictures, lettering, etc., transferred from paper to textile web by pressure with a hot iron), plasticizer, wire covering, pigment grinding base, safety glass ingredient, in lacquers, and textile coating material. J. W. H.

Economic and engineering trends in plastics. A. F. Randolph. *Chem. & Met. Eng.*, **44**, 25–8 (Jan., 1937).—The several hundred plastics that are commercially available are of fifteen to twenty types. Many changes occur in these from year to year.

Recent years have brought many advances in the quality of nitrocellulose used for plastics, and especially as an interlayer in windshield safety glass. This interlayer is now produced in the form of a continuous sheet. Cellulose acetate is proving even more popular than cellulose nitrate for this purpose.

Plastics are now being made into delicate and complicated shapes previously beyond the scope of any known technic.

Phenol-formaldehyde resins are now available in special types to meet particular purposes ranging from soap containers to brake linings.

Furfuraldehyde-phenol resins are proving very satisfactory and especially suited for injection and transfer molding. A bright future is predicted for this resin.

Some of the handsomest of recent commercial moldings are of urea-formaldehyde, and the fact it is available in translucent white and bright tints justifies its higher cost.

The much publicized soybean plastic utilizes the protein of this versatile bean in conjunction with phenol and formaldehyde. It is a heat-setting molding compound and superior in moisture-resistance to earlier protein plastics.

Many vinyl resins are being developed. The most interesting of the new resins are polymerized esters of acrylic and methacrylic acids. Many show complete transparency and can be colored to any desired shade. J. W. H.

Synthetic anti-malarials. W. O. Kermack. *Science Progress*, **30**, 457–9 (Jan., 1936).—Malaria is one of the major destructive diseases attacking the human race. In India, it is reckoned that 80–100 millions out of 370 millions contract this disease every year. The fight against it is being carried out on many fronts. Control of the disease has always been attempted by measures directed against the mosquito.

In recent years a vigorous attempt has been made to attack the malaria problem from a new angle. The efficiency of quinine as a specific for malaria has been known since the seventeenth century. Though relatively cheap, the quinine alkaloids are still too dear to allow their free use by poverty-stricken multitudes among whom the disease is so rampant. It is no surprise, therefore, that attempts should have been made to manufacture compounds more or less closely related to quinine, in the hope of obtaining a drug with all the efficiency and none of the disadvantages of the natural alkaloid. The problem is complicated because the parasite has curious and complex ways. There are three distinct types of parasite, subtertian, benign tertian, and quartan. What is needed is a drug which will attack each of the forms of each of the parasites with complete and certain effect and at the same time be so specific as to leave the tissues of the host quite unharmed.

Two anti-malarials have become best known during recent years, namely, plasmoquin and atebrin. The former is a quinoline and the latter is an acridine derivative. Plasmoquin, it would seem, has not fulfilled its early promise. In the case of quartan and benign tertian malaria it is doubtful whether it has any advantages over quinine. It is definitely not suitable for the general treatment of malaria. It is rather treacherously toxic and, moreover, fails to deal with the asexual form of the subtertian parasite. Atebrin, on the other hand, would seem to be in almost every way as effective as quinine and to be definitely superior in reducing the number of relapses.

It is stated that 12,000 different compounds were prepared and tested by the I. G. German chemical combine in the course of the development of plasmoquin and atebrin. This indicates the magnitude of the effort required. R. K. C.

Trends in organic chemicals from petroleum and natural gas. B. T. BROOKS. *Chem. & Met. Eng.*, **44**, 18–21 (Jan., 1937).—In a broad sense any organic chemical that can be made by synthesis can be made from the paraffins, olefines, and aromatic hydrocarbons derived from petroleum. This paper discusses those which are now, or give real promise of being, manufactured on a commercial scale.

Butadiene, which is present along with a mixture of other close-boiling hydro-carbons in the C_4 fraction from cracked petroleum can be selectively removed and polymerized into high boiling oils and resins. In Russia a serious attempt is being made to make rubber from butadiene. Isobutene which is also in this C_4 fraction is made into tertiary butyl alcohol.

It has recently been shown that it is possible to produce two to three times as much toluene as benzene from petroleum. Much work has been done on producing acetylene by the gaseous decomposition of gaseous hydrocarbons at high temperatures. Acetic acid is made from the acetylene.

A plant has just been completed for making gasoline of high octane value by the polymerization of propane and butane.

Ethylene made by cracking petroleum is now used to make ethanol and ethylene glycol.

Propylene from cracked gasoline is made into isopropyl alcohol, which in turn is being made into isopropyl ether and acetone. J. W. H.

Phosphorescence and phosphors. A. J. MEE. *Science Progress*, **30**, 635–43 (Apr., 1936).—The phenomenon of luminescence has been known for centuries. The fact that plants and animals, usually of a lowly order, glowed in the dark, must have been observed by the earliest naturalists, and indeed, Pliny records certain instances of it, including that of the bivalve, *pholas*. In the majority of cases, the luminosity appears to be developed for the purpose of attracting the opposite sex, though in some cases it acts as a warning signal. Of all animals, the glow-worm appears to give the greatest intensity of light, the reason being that its glow has a maximum intensity at a wavelength of 5700 Å, which is the wave-length to which the human eye is sensitive.

It is important scientifically to distinguish between fluorescence, phosphorescence, and chemiluminescence, all of which are included under the heading of phosphorescence. A remarkable thing is that some organisms will glow only if they have been kept in darkness. A case in point is that of the ovoid jelly "Beröe." This is the direct reverse of true phosphorescence.

Even at the time when phosphorus was discovered, other inorganic substances were known which would glow in the dark, and these were the true phosphors. One, known as Baldwin's phosphorus, made by fusing calcium nitrate and then allowing it to solidify, was prepared by Baldwin in Saxony in 1674. Another, known as Bologna phosphorus was discovered by the Italian alchemist, Casciarola, while searching for the "philosopher's stone."

Despite their antiquity, inorganic phosphors have remained a scientific curiosity until recent times. Much of our present knowledge of phosphors is due to the German physicist, Lenard. In general a Lenard phosphor is made by fusing the sulfide of an alkaline earth metal with a flux, which itself plays no part whatever in the production of the phosphorescence but merely aids fusion. The composition of a few typical Lenard phosphors is given below: 1 g. $CaSO_4$ + 0.0004 g. Sb + 0.2 g. Na_2SO_4 + 0.06 g. NaCl; 1 g. $SrCO_3$ + 0.001 g. Bi + 0.06 g. MgF_2; 25 g. $BaCO_3$ + 15 g. Sr $(OH)_2$ + 15 g. S + 3 g. starch + 1 g.; MgO + 1 g. Li_2SO_4 + 2 cc. 0.5 per cent. solution of $ThSO_4$ + 3 cc. 0.4 per cent. $CuSO_4$.

The color of light emitted by a phosphor varies with the added heavy metal. Thus phosphors containing bismuth and thallium give a violet light; those containing bismuth and rubidium give a deep blue light. The light emitted by a phosphor always is of greater wave-length than absorbed light. In the majority of cases, the spectra show two or three emission bands, and these can often be separately excited, or at any rate selectively strengthened by altering the conditions of preparation of the phosphor.

Phosphors have found a number of uses. That with which the layman is most familiar is in luminous paint. Such paint consists of a Lenard phosphor, usually calcium, barium, or zinc sulfides, mixed with a minute amount of a radioactive substance, without which the flow would die out, to be renewed after further illumination. In the scientific world, phosphors, especially zinc sulfide and barium platinocyanide, have been used for making X-rays, cathode rays, and X-rays "visible." These radiations excite phosphorescence in these phosphors, and the tracks of the rays are then easily seen. The use of barium platino-cyanide screens in X-ray work before X-ray photography was developed is well known, and it must be remembered that Rutherford counted the α-particles emitted from a radioactive preparation by observing the scintillations produced when the particles struck a zinc sulfide screen. R. K. C.

For scholarly readers. ANON. *Ind. Bull. of Arthur D. Little, Inc.*, **120**, 1–2 (Jan., 1937).—A means of recording, storing, and distributing the written word, said to be the "most important discovered since the time of Gutenberg," is being developed in the form of a microfilm. A book, newspaper, or manuscript page is photographed on a microfilm minified to perhaps as little as two thousandths of its original area, thus preserving invaluable records on a film which the Bureau of Standards reports is comparable to paper in its permanency. 1937 is expected to see the first commercial introduction of acceptable equipment by libraries. The magnifying and reading mechanism is the present limiting factor. The film must not be scratched or overheated. The leading optical companies are actively interested in inexpensive devices for individual users. It has been suggested that film books be printed. Through microfilms valuable material the world over becomes available. The best organized microfilm service now available is that offered by the documentation division of Science Service, through which the extensive library of the Department of Agriculture may be drawn upon at a nominal fee. Industrialists see in the microfilm a new tool for their engineering and research departments. Foreign and domestic material may be tapped more readily. Already universities have taken the first step in using microfilms. The librarian at the University of Chicago is chairman of the microfilm committee of the American Library Association. It takes little imagination to visualize the possibilities of this new treatment of the written word. G. O.

HISTORICAL AND BIOGRAPHICAL

The early history of phosphorus. J. R. PARTINGTON. *Science Progress*, **30**, 402–12 (Jan., 1936).—The accounts in the textbooks of the discovery and early history of phosphorus are rather unsatisfactory and contradictory. The author brings to light a number of interesting facts which have hitherto not been emphasized. He quotes from various original sources, many of which are old, and thereby provides the reader with much valuable reference material.

The results of the author's investigation may be summed up as follows:

1. Phosphorus was discovered in 1674 or 1675, probably 1675, by Brand of Hamburg by a process depending on the distillation of evaporated urine. He prepared the solid, but only in small quantity.

2. At the end of 1675, or early in 1676, the process was sold to Krafft by Brand, who also informed Kunckel and at least one other person (a woman) that phosphorus was obtained from urine.

3. Phosphorus was obtained in the solid form from urine by Kunckel not later than March 1676, after a few weeks of experimenting.

4. The first description of phosphorus was published in 1676 both by Kirchmaier, whose information was derived from Kunckel, and by Elsholtz of Berlin who seems to have been in touch with Krafft. The latter publication was known to, but not seen by, Boyle.

5. Solid phosphorus in a pure state was exhibited to Boyle and others in September, 1677, by Krafft who told Boyle that it was obtained from "part of the human body." Boyle succeeded in 1680, after obtaining some further information from a German doctor, "A. G.," perhaps Hankwitz, in preparing an aqueous solution or suspension of phosphorus and in 1681 had obtained solid phosphorus. Boyle was the first (1680) to publish the

method of preparation, which appears to be that originally used by Brand, and is also that described in 1683 by Lemery, and in 1692 by Homberg, the latter obtaining his information from Kunckel.

6. The account of the discovery given by Kunckel in 1716, apart from an incorrect date, appears to be the true one, although it disagrees in part with those given by Leibnitz (1710) and Stahl (1731), both of whom knew personally some of the persons concerned, and whose accounts differ from one another.

R. K. C.

THE PHILOSOPHY OF EDUCATION

Research in higher education. F. PAYNE. *J. Higher Educ.*, **8**, 59–63 (Feb., 1937).—Mr. Payne says, "Science progresses most rapidly when precise measurements can be applied, and so it might be said that the advancement of science depends upon the development of methods of measurement. If, then, we wish to advance education from the point of view of science, the greatest need of research in higher education is in the field of measurement. Yes, I know these questions are difficult, and methods of approach may not now be available, but these are not good reasons for evasion.

"I have said that to educate means to lead—but where and by what route? I have implied that the leaders are having difficulties in charting and following their courses. They try one course and, without actually knowing whether they have succeeded, retrace their steps and start in a new direction. These changes are constantly going on and probably under present conditions should be encouraged. How else, other than by trial and error, are we to find our way? But even then how are we to find it if we do not know when we arrive? Can scientific studies help us? Certainly they should contribute to a better understanding of the problems, but does not the solution of the problems depend, first of all, upon a well worked-out philosophy of education? I am not thinking of a philosophy such as the political leaders of Germany, Russia, and Italy have forced upon their people, but of a philosophy for our American democracy—a philosophy broad enough to include tolerance; which recognizes young men and women as individualities to be developed in accordance with their abilities and interests, whether in college or out; which recognizes that there are diverse ways of accomplishing this result; and which recognizes that the student develops best as a result of his own efforts. This philosophy should also recognize that the welfare of the people at large is as vital as that of the individual; that the social and individual problems are constantly changing; and hence that our philosophy must also change. Above all, indoctrination is to be avoided."

A. T. B

The inception of a tutorial plan. H. F. FLETCHER. *J. Higher Educ.*, **8**, 33–8 (Jan., 1937).—For a number of years a group in the College of Liberal Arts and Sciences at Illinois has been much interested in the general problem of providing greater opportunities for the superior students in this college.

A number of studies were launched four or five years ago, the development and completion of which were essential to the formation of the problem as it was finally stated. One important development from these studies was the attempt to secure some other basis for the evaluation of the work of the student than the credit-hour and the marking system. The use of the credit-hour for the past two generations seems to put too great an emphasis on the quantitative aspect of student achievements, and too many students and faculty members think of undergraduate education almost entirely in terms of the number of credit-hours amassed and marks secured. The particular objection to this system was that something more than credit-hours and marks should be involved in evaluating the accomplishment of the superior student, and also that such a system was impractical in the development of the tutorial plan.

Many departments were desirous of establishing uniform comprehensive examinations for all tutorial students in the college. The point of view encountered in the departments of chemistry and zoölogy, and especially in the former, was that there has developed in the past generation a high type of honors work for the better students in chemistry, which has had a high degree of success. This department felt that it did not wish to impose the requirement of general comprehensive examinations on its superior students. Moreover, the members of the Department felt strongly that although their better students could profit a great deal from working under the tutorial system, the best results could be obtained by eliminating required courses and increasing for the individual student the amount of work that could be called tutorial work. In other words, their desire was for a greater degree of specialization for the student able to profit by it.

Mr. Fletcher says, "The outcome of the discussion and experimentation has been the adoption of a tutorial plan by the college faculty. This plan established a college tutorial committee in general charge of tutorial work and empowered to draw up detailed recommendations to be presented to the faculty of the college. It permits selected students recommended by departments, usually through some individual staff member and approved by the College Tutorial Committee, to proceed with their education in a flexible fashion."

A. T. B.

Accredited engineering schools. ANON. *J. Higher Educ.*, **8**, 50–1 (Jan., 1937).—The Engineers' Council for Professional Development, composed of seven national engineering societies, made public toward the end of October its first general list of accredited engineering schools. Hitherto, the only accredited list of engineering schools available has been drawn up by government officials. The new council now takes over this responsibility. The council is composed of the following societies: American Society of Civil Engineers, American Institute of Mining and Metallurgical Engineers, American Society of Mechanical Engineers, American Society of Electrical Engineers, Society for the Promotion of Engineering Education, American Institute of Chemical Engineers, and National Council of State Boards of Engineering Examiners.

The approved institutions and engineering curriculums are as follows:

Brown University—civil, electrical, mechanical.
Carnegie Institute of Technology—chemical, civil, electrical, management, mechanical, metallurgical.
Clarkson College of Technology—civil, electrical, mechanical.
College of the City of New York—civil, electrical.
Columbia University—chemical, civil, electrical, industrial, mechanical, metallurgical, mining.
Cooper Union Institute of Technology—civil, electrical, mechanical.
Cornell University—administrative, chemical, civil, electrical, mechanical.
Dartmouth College—civil.
University of Delaware—civil, electrical, mechanical.
Drexel Institute—chemical, civil, electrical, mechanical.
Johns Hopkins University—civil, electrical, mechanical.
Lafayette College—civil, electrical, mechanical, metallurgical, mining.
University of Maine—civil, electrical, general, mechanical.
Massachusetts Institute of Technology—aëronautical, architectural, business and engineering administration, chemical, civil, electrical, electrochemical, general, mechanical, metallurgy, mining, naval architecture and marine, sanitary.
University of New Hampshire—civil, electrical, mechanical.
New York University—aëronautical, chemical, civil, electrical, mechanical.
Newark College of Engineering—civil, electrical, mechanical.
Norwich University—civil, electrical.
Pennsylvania State College—architectural, chemical, civil, electrical, electrochemical, industrial, mechanical, sanitary.
University of Pittsburgh—chemical, civil, electrical, industrial, mechanical, metallurgical, mining, petroleum.
Polytechnic Institute of Brooklyn—chemical, civil, electrical, mechanical.
Princeton University—chemical, civil, electrical, mechanical.
Rensselaer Polytechnic Institute—chemical, civil, electrical, mechanical.
Rhode Island State College—civil, electrical, mechanical.
University of Rochester—mechanical.
Rutgers University—civil, electrical, mechanical, sanitary.
Stevens Institute of Technology—general.
Swarthmore College—civil, electrical, mechanical.
Syracuse University—civil, electrical, mechanical.
Tufts College Engineering School—civil, electrical, mechanical.
Webb Institute of Naval Architecture—naval architecture and marine.
Worcester Polytechnic Institute—civil, electrical, mechanical.
Yale University—chemical, civil, electrical, mechanical, metallurgical.

A. T. B.

RECENT BOOKS

DE LA MÉTHODE DANS LES SCIENCES EXPÉRIMENTALES. *Henry Le Chatelier*, Member of the Institute, Professor in the Faculty of Sciences. Dunod, 92 Rue Bonaparte (VI), Paris, 1936. 319 pp. 13.5 × 21.0 cm. 21 fr. 05.

The present book contains in a different form the same ideas as the book entitled SCIENCE ET INDUSTRIE which Le Chatelier published shortly after the war, the most important difference being that he here takes from his own work the examples with which he illustrates the various rules of the methodology of science. The reader will be glad that he has done this. The author, naturally, is able to speak with the greatest authority when he speaks concerning his own work. He gives us the mature conclusions of a seasoned veteran. The book has proved to be Le Chatelier's valedictory. Born October 8th, 1850, he died September 17th, 1936.

The central purpose of the book is to emphasize the interdependence of science and industry. "I have consecrated my whole career to industrial science," writes Le Chatelier, "not because of a reasoned wish but because of the impulsion of exterior circumstances. In my youth I never heard mention of the distinction between pure science and applied science." His father was attached to the *Credit Mobilier* and directed the construction of railroads. He retained from his school days an interest in chemistry, and had a laboratory in his home. He was intimate with Henri Sainte-Claire Deville and often took his son to the laboratory at the *École Normale* where he heard discussions on the fusion of platinum and the manufacture of aluminum. "The researches of Sainte-Claire Deville, which will forever make his name illustrious, seemed, at the very moment when he was pursuing them, to occupy a less important place in his thought than his industrial studies."

On completing his course at the *École Polytechnique*, Henry Le Chatelier, because of his rank in his class, was sent to the *École des Mines* with the title of *Ingénieur de l'Etat*. Two years after graduating from the latter school he was "bombardé professeur de chimie"—shot into the position of professor of chemistry—at the *École des Mines*, a fact which he ascribes to the benevolence of Daubrée, the Director of the school and a friend of his father, and immediately set to work to prepare himself properly to fill the position. "Not knowing how to orient my first work," he writes, "I thought of my father's old friend, Sainte-Claire Deville, and went to ask him his counsel. He received me badly and made fun of me, saying that my question was absurd. When a man works in the laboratory, he is assailed by a multitude of problems, and his only difficulty is to make a judicious choice among them. I had only to get to work, to do anything at all, and I would soon encounter interesting questions." Le Chatelier remembered certain briquettes of hydraulic cement which his maternal grandfather, Pierre Durand, had made and decided to study the composition of these materials. The work was his Doctor's thesis. The study required the exact determination of high temperatures, for which no satisfactory method was known. Le Chatelier was successful in using thermocouples for the purpose, these having been suggested fifty years earlier by Antoine Becquerel, but never applied, having been formally condemned by Regnault. Following this he devised an optical pyrometer for the measurement of temperatures above the melting point of platinum, and made the first determinations of the temperatures which are realized in the cement, metallurgical, ceramic, and glass industries. Because of the phenomena which these researches brought to his attention, he devoted himself for a number of years to the study of the principles of chemical equilibrium.

Explosions were frequent in gaseous coal mines; many lives were lost annually; the French government appointed a commission to study the matter—and the technical part of the work was put in the charge of two professors at the *École des Mines*, Mallard and Le Chatelier. As part of a theoretical study of combustion they measured for the first time the variations in the specific heats of methane and other combustible gases at elevated temperatures. Le Chatelier on his own account also studied the combustion of actylene and suggested the use of the oxyacetylene blowpipe for the autogenous welding of steel. At the suggestion of Mallard he undertook a study of the allotropic modifications of certain minerals, and discovered the anomaly in the dilatation of quartz at 570°. He studied amorphous silica, tridymite, and cristobalite, the latter reputed to be a rare mineral, but showed that cristobalite is in reality the principal material of the silica bricks which are used in steel furnaces.

Le Chatelier was persuaded by Lan, newly appointed Director of the *École des Mines*, to take charge of the course in metallurgy. This led him to study alloys, to develop microscopic metallography, and finally to enunciate the general theory of alloys which is definitively accepted today. Finally, in order to diffuse the new scientific notions, he founded with the help of a committee of steel manufacturers, the new periodical, *Revue de Métallurgie*—which still further extended his relations with industry.

When Le Chatelier, still retaining his position at the *École des Mines*, accepted the chair of chemistry at the Sorbonne which had been made vacant by the death of Moissan, he found himself without time for work in the laboratory. In consequence of an article in the *Revue de Métallurgie* relative to the work of the American engineer, Frederick Winslow Taylor, on fast-cutting steels, Le Chatelier entered into a correspondence with Taylor and became informed concerning his formulation of the principles of factory organization (the Taylor System). He was passionately interested in these questions, and during twelve years published many papers in which they were discussed.

At the request of the military authorities during the war, Le Chatelier again turned his attention to the study of refractory materials, to metallurgical questions, and especially to the problem of tempering projectiles. His knowledge of the procedure of science and of the organization of the forces of production served his country in good stead. He retired from active work at the age of seventy shortly after the signing of the peace. . . . "During my fifty years as professor at the *École des Mines* I have always thought that the function of a professor does not consist merely in teaching his students the results which science has acquired, but that he ought to make efforts to inculcate in his auditors a confidence in the use of the scientific method and so to develop their intellectual faculties instead of seeking only to equip their memory. In retirement today, and no longer having the professor's chair at my disposal, I have wished to continue by pen what I am no longer able to do by word of mouth."

The foregoing is a summary of the Introduction, and it also indicates sufficiently the sort of material which comprises the body of the book and supplies the author with evidence for his methodological conclusions and with support for his thesis of the interdependence of science and industry. The actual chapter headings are as follows: I. Definition of Science; II. General Principles; III. The Observation of Facts; IV. Mechanism of Discovery; V. Experimental Measurements; VI. Apparatus for Observing and Measuring; VII. Errors; VIII. Reasoning; IX. Laws; X. The Industrial Origin of Science; XI. Influence of Science on Industry; XII. Introduction of Science into the Factory; XIII. Discoveries and Inventions; XIV. Scientific Teaching; XV. Technical Teaching; XVI. The Taylor System; XVII. Conclusion.

The book is important, intelligent, stimulating, and provocative—a book to be chewed and digested.

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INORGANIC CHEMISTRY, A Survey of Modern Developments. *Sir Gilbert T. Morgan*, D.Sc., Sc.D., LL.D., F.R.S., F.I.C., A.R.C.Sc., Director of Research, and *Francis H. Burstall*, M. Sc., A. I. C. of the Chemical Research Laboratory, Teddington, Middlesex, Department of Scientific and Industrial Research. W. Heffer and Sons, Ltd., Cambridge. Special First American Edition, Chemical Publishing Co., 148 Lafayette Street, New York City, 1937. ix + 462 pp. 18 figs. 10 tables. 14 × 22 cm. $6.00.

This excellent book "is an amplification of the subject matter of three lectures embodying a survey of modern inorganic chemistry." "For the purpose of this treatise, which is of a recapitulatory character, we propose to regard the scope of inorganic chemistry as a study of the chemical elements, other than carbon, including within this purview a typical selection of the diverse combinations assumed by many of these elements." While a discussion of the compounds of carbon is omitted, for obvious reasons, the authors explain that "it is undesirable to exclude all references to carbon derivatives, for such organic components frequently throw considerable light on the nature and constitution of complex inorganic material."

In carrying out this plan, the introductory chapter discusses the present conception of the term element, together with a review of atomic structures, radioactivity, isotopes, nuclear structures, and the newer notions concerning valence. Then follow ten chapters which are devoted to the various groups of chemical elements. In these chapters brief summaries are given of the recent additions to our knowledge of the chemistry of all the elements. The selection of material for such a summary is a difficult task for any author, because of the bewildering abundance of material available. The present book shows keen discrimination in the choice of subject matter. It is obvious that a book of this scope could not be expected to give, even in summary, a tabulation of all the developments of recent years in such fields as the applications of inorganic materials to engineering. To avoid such a voluminous compilation the authors have chosen stimulating topics particularly from the standpoint of theoretical studies.

The last eight chapters are devoted to the following topics: Transmutation of the Elements; Coördination Compounds; Corrosion of Metals; Intermetallic Compounds; Carbides; Metallic Carbonyls; Netrosyl Compounds; and Organic Derivatives of Metals and Metalloids. These are all topics of consuming interest to the inorganic chemist, and the authors have made an outstanding contribution by giving in a clear, concise form these summaries of present-day subjects. The discussions are clearly stated, the explanations are easily followed, and each topic, in turn, is developed skilfully and understandingly without voluminous technical detail. Throughout the discussions the interest of the authors in coördination compounds is very evident. It is fortunate to get a summary of these studies and their applications by such outstanding authorities.

This book appeals to the reviewer as one of the most outstanding contributions of recent years to the subject of inorganic chemistry. It makes no pretense of being a compendium of recent developments, but it does summarize in splendid form the present theories and modern viewpoints. It will be invaluable to advanced students in chemistry, to all who wish to keep in touch with the developments in this field and to those who desire a clear, concise summary of modern thought. It is outstanding as a convenient and dependable reference book, and, if the price were more reasonable, it would be an excellent textbook for use in courses devoted to the recent advances in theoretical inorganic chemistry.

There is no appendix in the book, and specific references to original sources of information are not given. The compilation of a suitable bibliography for such a work would be a task of no mean proportions. It would add greatly to the bulk of the volume. The names of contributors are given, and the years of discovery are included. The authors suggest that "such brief references should suffice as guides to those students who wish to extend their reading to original memoirs without rendering the treatise too bulky for general readers who would be content with a more condensed epitome of contemporaneous investigations." Both name and subject indices are given.

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ESSENTIAL PRINCIPLES OF ORGANIC CHEMISTRY. *Charles S. Gibson*, Guy's Hospital Medical School, University of London. University Press, Cambridge, 1936. viii + 548 pp. 43 figs. 14 × 22 cm. $5.00.

This book is a beginning text in organic chemistry intended for those who will eventually specialize in the subject, or for those who will later engage in such sciences as biochemistry, physiology, pharmacology, and therapeutics. The author has adopted the plan of discussing aliphatic, aromatic, and heterocyclic compounds together. Although this plan has advantages, there are obvious drawbacks. It requires one-sixth of the book (the first eighty-four pages) to deal with hydrocarbons. In the author's outline he found it necessary to discuss completely such topics as these before coming to alcohols, aldehydes or acids: cyclic hydrocarbons, cis-trans isomerism, proof of the equivalence of the six hydrogens of benzene, Körner's method of establishing orientation, naphthalene (including the synthesis of α-naphthol from phenylisocrotonic acid), anthracene, and phenanthrene. Generally, the presentation has been satisfactory, but it seems to the reviewer that this approach is better adapted for review purposes than for an initial introduction to the subject.

There are many places in the book where earlier presentation of subject matter would have assisted materially. Perhaps the most outstanding example is that of the Grignard reagent, which is not mentioned until seven pages from the end of the book.

One would expect a text which is designed for future biochemists, pharmacologists, etc., to mention such subjects as ephedrine, carcinogenic hydrocarbons, dihydric phenols and phenolic germicides, anthocyanins, or "essential" amino acids, but no mention is made of such matters. Chlorophyll and hemoglobin are dismissed in one sentence, and only one-half page is devoted to sterols. Except for the passing mention of vitamin D under sterols, no mention is made in the book of any of the vitamins. There are equally serious omissions in the text from the standpoint of students "who will eventually specialize in organic chemistry." For example, no reference is made to triphenylmethyl or cyanine dyes. Triphenylmethane dyes are noted in the index, but this entry turns out to be nothing but a statement that phosgene may be used in their manufacture. One looks in vain also for mention of the Diels-Alder reaction, or of the industrial synthesis of phenol from chlorobenzene, or of the industrial manufacture of acetic anhydride from acetic acid and ketene. *i*-Propyl ether is not mentioned, nor is any account given of the recent industrial development of ethylene and propylene as raw materials. As a matter of fact, on page 98 it is intimated that the preparation of ethanol from ethylene is not practical. Workers in the petroleum industry would object to the statement that the source of industrial ethylene is gas "from the coke-oven plants."

In most cases the author has used good nomenclature. There are occasional moments of laxity, however, as witnessed by the use of methylethyl ketone (pages 110 and 223), 2-methyl-*n*-butyl alcohol (page 112), methylphenyl ether (page 130), acetophenoneoxime (page 189), and allyl for $-CH{=}CHCH_3$ (page 301). Dots and bonds are used interchangeably in structural formulas, a practice which leads to confusion in cases where electron formulas are included (as on pages 259 and 267). It would be confusing even if the reader were warned that a bond may be represented by one dot or by two dots, but no such warning signal is sounded.

Objection may be made to the author's preference for the meso-bridge formula for anthracene (page 81), or for the C-O-S type of structure assigned to bisulfite addition products of aldehydes (page 156), or for the mechanism of Skraup's reaction (page 302) wherein $C_6H_5N{=}CH{-}CH{=}CH_2$ is assumed to be

an intermediate. Objectionable also is the fact that the outdated Crum-Brown and Gibson rule is the only help given the student on the matter of orientation. Molecular rearrangements are treated much too casually. The reader is introduced to this subject in a footnote (page 107) during the discussion of pinacol and pinacolone. There is no comment other than to call it "a remarkable intramolecular interchange." The next rearrangement is the Kolbe synthesis of salicylic acid. No longer is this considered to be remarkable, but it is spoken of merely as "an intramolecular change." It would seem that the author should give the student more enlightenment on the processes involved.

One final criticism is that the book reflects an unfortunate nationalistic bias. Of approximately seventy references which are made to the work of chemists who are now living, about sixty of these are references to the work of British investigators.

This book is attractively bound and well printed. It should be helpful to students in their supplementary reading. As a textbook of elementary organic chemistry, however, it impresses the reviewer as being definitely inferior to many which are now available.

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PREPARATION OF SCIENTIFIC AND TECHNICAL PAPERS. *Sam F. Trelease*, Columbia University, and *Emma Sarepta Yule*, University of the Philippines. Third edition. The Williams and Wilkins Co., Baltimore, Md., 1936. v + 125 pp. 12 × 18.5 cm. $1.50.

This is the third edition of a well-known book which should be available to every student who writes articles or reports on scientific or technical subjects. It is primarily a reference book on matters relating to style and form and the mechanical construction of a scientific or technical report. Some of the topics covered are: suggested outlines, suggestions on subject matter and arrangement, use of tenses, capitals, abbreviations, construction of tables, literature citations, abbreviations for scientific publications, use of headings, proof reading, and illustrations.

The purpose of the authors is well accomplished, and this little book answers almost any question pertaining to form which the prospective author of a technical report might put to it.

The author states in the preface, "This handbook is not a manufactured product, not a collection of theories; it grew." To this reviewer it appears that some pruning of overgrown branches and some building up of undernourished ones would have added considerable value to this vegetative book. For example, seventeen pages are devoted to a description of four different methods of literature citations, and only five pages to general suggestions on subject matter and arrangement. A more symmetrical structure might have grown if the various branches and twigs described so well had been bound together in closer relation to the main stem. In short, the reviewer believes that the book lacks an adequate treatment of subject matter and of the technic of developing the several sections of a report.

ALTON L. KIBLER

EDGEWOOD ARSENAL
EDGEWOOD, MARYLAND

LABORATORY GUIDE TO THE STUDY OF QUALITATIVE ANALYSIS. *E. H. S. Bailey*, Ph.D., and *Hamilton P. Cady*, Ph.D. Tenth edition, revised by *Arthur W. Davidson*, Ph.D., Associate Professor of Chemistry in the University of Kansas, in collaboration with the junior author. P. Blakiston's Son & Co., Inc., Philadelphia. xiii + 322 pp. 2 figs. 1 chart. 15 × 22 cm. $2.00.

According to "Who's Who in America," this book was first published in 1901, although even then it appears to have been a revision of an earlier book, very similar in title, which was published by Bailey and Cady in 1896 and had already gone through three editions. In 1901, Dr. Bailey was about fifty-three years old and Dr. Cady was a youth of twenty-five. Before going to Kansas Dr. Bailey had had teaching experience at Yale and at Lehigh. He died in 1933.

The idea of having two men coöperate in preparing a textbook is usually a good one, particularly when one of the men is an experienced teacher and the other is a youth enthusiastic about new ideas. For that reason, the book by Bailey and Cady was one of the first to attempt to teach qualitative analysis on the basis of the Ionization Theory of Arrhenius and the Mass Law of Guldberg and Waage. By continuing this practice of having a young instructor active in revising the book, it has been kept up to date during these forty years. Paul V. Faragher prepared the eighth edition, and Arthur W. Davidson the ninth and tenth.

A study of the curricula of about one hundred fifty colleges and technical schools of the United States shows that it is common practice to devote relatively little time to laboratory practice in qualitative analysis. In many cases, the course is merely a part of the first year instruction. The book of Bailey and Cady, in its revised form, is more than adequate for all such courses. Most teachers will like the way in which the subject of the "oxonium" ion is discussed. The book states that "a hydrogen ion certainly combines with at least one molecule of water to form the complex ion $H(H_2O)^+$ or H_3O^+ which is called the oxonium ion" but, since the exact extent of hydration of the ion is not very well known, the authors continue to write the chemical formulas of ions in solution as if they were anhydrous.

The book makes note of the marked differences between strong and weak electrolytes, and the limitations of the Mass Law are taken into consideration. The procedures have been modified somewhat, and some new tests described. About half the book has printing on the left-hand pages only, and the right-hand pages are available for additional notes, or for writing balanced equations to illustrate the reactions studied. Teachers who have used the manual with their classes will undoubtedly welcome the new edition. It is well-written, and its doctrine is sound.

WILLIAM T. HALL

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

THE DRAMA OF CHEMISTRY. *Sidney J. French*, Assistant Professor of Chemistry, Colgate University. The University Society, Inc., 468 Fourth Avenue, New York City, 1937. vii + 170 pp. 112 figs. 15 × 23 cm. $1.00 net.

This book is one of The University Series the purpose of which "is to present, in an attractive form and in a concise, readable style, the truly amazing story of the life of mankind—an authoritative survey of the physical and social sciences, history, philosophy, literature, and the arts. The books are not intended to be textbooks or to treat any subject in confusing detail." Professor French has done exceedingly well by chemistry in his contribution to this series.

"The Drama of Chemistry" is developed historically with particular emphasis on theory in ten concise chapters; *viz.*, Early History, The Awakening of Chemistry, The Chemical Revolution, The Era of Empiricism, The Theory of Ions, Structure of Atoms and Molecules, Organic and Biological Chemistry, Chemistry and Civilization, The Chemist and His Work, and The Future of Chemistry. Appended are suggestions for future reading, a glossary, and an index.

Thoroughly modern in outlook, such topics as the modern revisions of the dissociation theory, wave mechanics, polar molecules, and nuclear chemistry are treated in an understandable fashion. For accomplishing so much so well in so few pages, the author is to be congratulated.

The reviewer recommends this book for collateral reading in elementary chemistry courses and as the chemistry unit in general science survey courses. Both the student and the teacher will enjoy using it.

JOHN A. TIMM

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TRADE ANNOUNCEMENTS

Welded Alloys Rolled to Infinitesimal Thickness

Strips of two alloys, copnic and chromel, were welded together and rolled to a thickness of six millionths of an inch recently in the laboratories of the *General Electric Company*. Even when magnified two hundred fifty times the weld in the ultra-thin bimetallic foil can be distinguished only by the difference in color between the two alloys.

The six millionths of an inch thickness was achieved by placing the welded strips of the two alloys—the one of copper and nickel and the other of chromium and nickel—between pieces of steel and reducing the combination as a unit by passing it between rolls. The final product of the rolling process is as delicate as gold leaf and must be handled with equal care.

The two alloys might have been lap welded after being rolled, according to engineers in charge of the work, but such a procedure would not have given the same clean appearance and uniform characteristics. Rolling is the only method known by which such extreme and uniform thinness can be obtained in metals.

New Folder Describes Stokes Water Stills

An eight-page leaflet just issued by the F. J. Stokes Machine Company of Philadelphia describes briefly their line of laboratory and smaller industrial type water stills. Attractively printed in two colors, it contains illustrations of the various models, specifications and prices. Special attention is given to the No. 171 one-gallon per hour laboratory still which is the latest model built by this company.

"Handbook of White Pigments"

A "Handbook of White Pigments," prepared by the *Krebs Pigment & Color Corporation* to make available to pigment users a convenient book of reference, is ready for distribution. It describes each of the company's white pigments briefly, indicating its field of use, consistency, physical and chemical characteristics, and other pertinent information.

The handbook describes pigments under three headings: lithopone (zinc sulfide pigments); pure titanium dioxide; and extended titanium pigments. It also contains tables of bulking values of white pigments, a tabular summary of consistency range, special properties and principal uses of white pigments, and conversion tables giving comparison of metric and customary units.

New Brazing Alloy Increases Applications

Improvements and refinements in manufacturing Phos-Copper brazing alloy have been announced by the *Westinghouse Electric and Manufacturing Company*. Increasing its field of application, the new processes include annealing and pickling to insure freedom of any carbonacious deposit on the surface which might interfere with the production of leak-proof joints. This makes the new alloy especially suitable for applications such as refrigerator parts where leak-proof joints are a necessity.

An alloy of phosphorus and copper, developed to replace expensive silver solders, Phos-Copper has a relatively low melting point, high tensile strength, and excellent penetration. Some of its other desirable properties include absolute uniformity of alloy, self-fluxing properties for most applications, high ductility, high fatigue resistance, high corrosion resistance, high electrical conductivity, high fluidity at brazing temperature, and economical to use. Also, brazed joints may be electroplated or tinned.

Phos-Copper is applied essentially the same as soft solders, except Phos-Copper requires a higher temperature. It melts at 707° C., a temperature which can easily be obtained by an oxy-acetylene torch, incandescent brazing, or carbon arc. High fluidity at brazing temperatures makes the alloy easy to use.

New Research on Optical Glass at Mellon Institute

A broad program of fundamental investigations on the chemistry and physics of glass surfaces to aid in the development of scientific apparatus and ophthalmic instruments has been started at Mellon Institute of Industrial Research by the *Bausch & Lomb Optical Company, of Rochester, N. Y.* The first studies will be concerned with the effects of environmental factors on the durability of the various types of glass used in optical instruments.

The *Bausch & Lomb Optical Company*, whose research in optical glass dates from the initial work of William Bausch in 1912, has maintained a fellowship at Mellon Institute since 1931 for research on various plant and production problems in optical technology. New developments in the past have included improved greases for optical instruments, cements for ultra-violet transmitting optics, improved methods for making and testing mirrors and reflectors, and standardization of the sizes of fine abrasives used in grinding lenses.

"Precision" Midget Water Still

For laboratories whose distilled water requirements are not very great, but who need a dependable supply of freshly distilled water, the new "Precision" Midget Still of the *Precision Scientific Co., 1750 N. Springfield Ave, Chicago*, offers many of the same tested and proven principles of still design as exemplified in "Precision" laboratory type water stills in the larger sizes. Having been designed from the standpoint of the utmost simplicity for easy installation and operation, the "Precision" Midget Water Still practically runs itself, producing an automatic continuous supply of distilled water that is chemically, physically, and bacteriologically pure. The Midget Still needs no permanent piping connections; it can be installed instantly wherever a water supply and ordinary 110-volt A.C. or D.C. electric current are available. Water supply and drain connections are served adequately with rubber tubing.

After opening up the water supply and turning on the electric current, the "Precision" Midget Still operates automatically, producing a continuous flow of distilled water, demanding no further attention. The proper water level is automatically maintained in the evaporator by means of a constant level cup, and the excess water overflows to the drain.

Zin-O-Lyte

Grasselli Chemicals Department of *E. I. du Pont de Nemours & Company* has just issued a trade bulletin explaining the use of "Zin-O-Lyte," which, it says, is the one process for bright zinc plating producing brilliant deposits direct from the bath without bright dipping. The process operates with equal success in still plating or in barrel plating and is applicable to almost all types of iron and steel products except some types of castings.

Zinc deposits produced by this process possess those qualities required for the greatest rust protection. The deposits are ductile and firmly adherent. Molybdenum, in small amounts, co-deposited with zinc, produces a brilliant finish without bright dipping, a polished surface direct from the bath.

The Company has developed a process for the control of the corrosion of the zinc anode whereby the anode current efficiency is approximately the same as the cathode current efficiency, making it possible to hold the zinc content within normal limits. This, it is claimed, overcomes the difficulty formerly experienced with the gradually increasing zinc content of the electrolyte because of excessive anode corrosion.